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LVII. *The Separation of Isotopes and a Further Separation of Mercury by Evaporative-Diffusion.* By WILLIAM D. HARKINS, *Ph.D.*, *Professor of Physical Chemistry, University of Chicago*, and BERNARD MORTIMER, *Ph.D.**

I. INTRODUCTION : SEPARATION OF ISOTOPES BY
DIFFUSION.

THIS paper describes a method by means of which the isotopes of mercury may be partially separated by a process which is rapid in comparison with other processes which have been used elsewhere. The separation attained is of the order of 0.2 unit of atomic weight, but it would not be difficult, though it would be costly, to attain a separation of a unit if sufficient assistance were available for the work.

The only general method which has thus far proved successful in actually separating isotopes is that of diffusion. While a few isotopic atoms are separated from each other by the use of positive rays, they are almost immediately shot into paper or metal from which they cannot be segregated, so that no material, not even an unweighable amount, is separated. However, it seems probable that the current carried by the positive rays can be increased, at least with some elements, to such an extent as to give perceptible amounts of material. Isotopes may be separated by vaporization at a low pressure, but this is a diffusion process in which the surface acts as a membrane with pores of molecular dimensions.

* Communicated by the Authors.

The first work which was definitely shown to have given a separation of isotopes, that is. a change of the atomic weight of the element, is that of Harkins and Broeker*. They obtained an increase (ΔM) of 0.055 unit in the atomic weight of chlorine, in January 1920, by the diffusion of hydrogen-chloride gas through the walls of porous churchwarden pipe-stems at atmospheric pressure in the apparatus shown in fig. 1. The cut (C) was 8000, that is, the first of the final heavy fractions produced contained 1/8000 as much hydrogen chloride as was used for the initial diffusion. The procedure is shown diagrammatically in fig. 2. The materials used for the work were extremely pure hydrochloric and sulphuric acids, and sodium bicarbonate, and purifications were made both before and after the final diffusion. Five determinations of the change of atomic weight, made by an accurate method and arranged in the order of the determination, gave values (ΔM) of 0.052, 0.059, 0.057, 0.55, and 0.53 unit. Since intermediate purifications were made, and the hydrogen chloride was proved to be free from iodine and bromine, the fact that there is no general trend in one direction in the values shows that this was actually a separation of isotopes. The increase of atomic weight, based on the ordinary theory of diffusion, should have been 0.089, so the efficiency was 62 per cent.

Another separation begun even earlier, but completed later†, gave, with the same cut, an increase of atomic weight of 0.043 unit, or an efficiency of 48 per cent., while a separation of the light fraction‡ gave a decrease of 0.039 unit, with a mean efficiency of 66 per cent. These were both carried out by the use of churchwarden pipe-stems of the same general character as those used by Harkins and Broeker, and the general method used was the same.

An increase in the diameter of the pores of the pipe-stems decreases the efficiency. For example, in the second separation of the isotopes of chlorine§ a cut of 12,000 gave an increase of atomic weight of 0.040 unit, with an efficiency of 36 per cent. The diffusions were carried out with great care, but it was found that the pores in the walls of the porcelain tubes, which were prepared specially for the work by the Bureau of Standards, had larger diameters, as

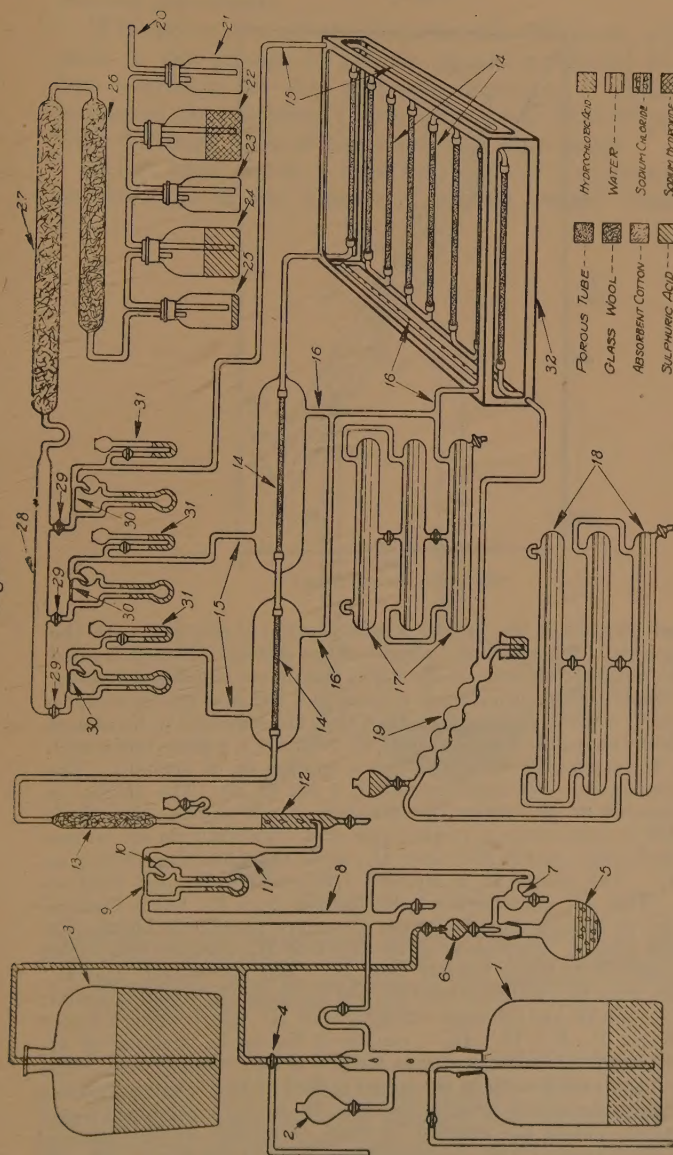
* 'Physical Review,' xv. p. 74 (Feb. 1920); 'Science,' li. p. 289 (1920); 'Nature,' cv. p. 230 (1920).

† Harkins & Liggett, J. Phys. Chem. xxviii. p. 74 (1924).

‡ Harkins & Jenkins, J. Am. Chem. Soc. xlviii. p. 58 (1926).

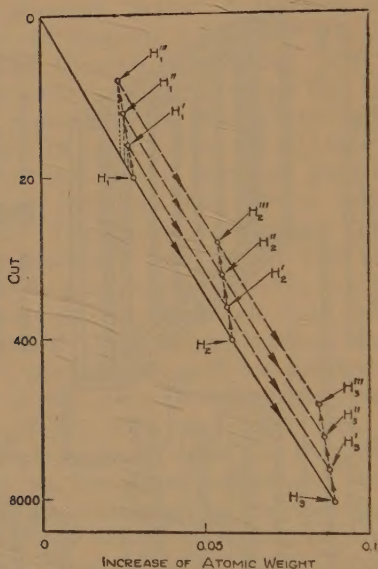
§ Harkins & Hayes, J. Am. Chem. Soc. xliii. p. 1083 (1921).

Fig. 1.



Apparatus used in the first separation into isotopes. Pure hydrogen-chloride gas, generated in flasks (1 or 5) on the left, passed through 12.2 metres of porous churchwarden pipe-stems (14), and the heavy fraction, which passed through the porous tubes, was absorbed by passing over water in the tubes 18. The first two tubes were inclosed in separate jackets, while the remainder were in the large glass case 32. A swift air-current passed in through 20-15.

Fig. 2.



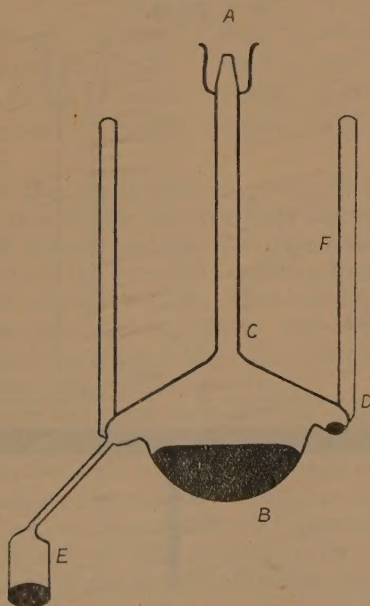
Theoretical increase of the atomic weight (x -axis) of chlorine with the cut (y -axis). The cut is the weight of the chlorine diffused divided by the weight of chlorine in the heavy fraction or undiffused residue. The number of the operation is plotted on a z -axis, so the lines represented by dashes, such as H_1'' , H_2'' , H_3'' , are supposed to lie almost vertically above the line O, H_1, H_2, H_3 with the x, y plane horizontal. This line is slightly curved, though it appears to be straight. The original sample (0) is diffused with a cut of 20. The residue is represented at H_1 , while the diffusate is not shown, since it is treated in such a way as to give cuts of 2. The sample H_1 is now diffused, with a cut of 20 to give H_2 , while the remaining 19/20 goes to H_1' . The sample H_2 is diffused, 1/20 going to H_3 , and 19/20 to H_2' . Thus H_2' contains the light fraction from H_2 , but it contains the heavy fraction from H_1' , since these are practically identical in atomic weight. As a result of the fact that H_2' contains two united fractions, it is much heavier than H_2 . For the reason that H_3' comes from H_2' , which is heavier, and H_3 from H_2 , which is lighter, the sample H' has 1.9 times the weight of H . The combined heavy fractions, H_3, H_3', H_3'', H_3''' , contain 9 times the material of H_3 alone, yet their average atomic weight is only slightly less. The cut of 8000 referred to in the paper is that of the heaviest fraction H_3 , while the atomic weights listed are those of the combined heavy fractions. Thus the greatest increase of atomic weight attained (for H_3) is slightly higher than that reported in the paper. The cut for H_1''' , for example, is given by the intersection of the dotted line from H_1''' and the line OH , that is, the point is the vertical projection of H_1''' on the x, y plane.

revealed by microphotographs, than those of the churchwarden pipe-stems.

With pores of a given diameter the efficiency, with reference to the change of atomic weight produced by a given cut, increases as the pressure decreases. Thus at low pressures the efficiency increased to from 90 to 98 per cent.*, with diffusion walls of churchwarden pipe-stems.

It has been shown† that the value of a separation varies as the cube of the change of atomic weight attained. If

Fig. 3.



Cross-section of evaporator.

Apparatus for the separation of mercury into isotopes by vaporization at low pressures. B, heavy residue; E, light condensate; A, mercury-sealed joint for connexion to vacuum-pump; F, Dewar jacket for holding ice used for cooling.

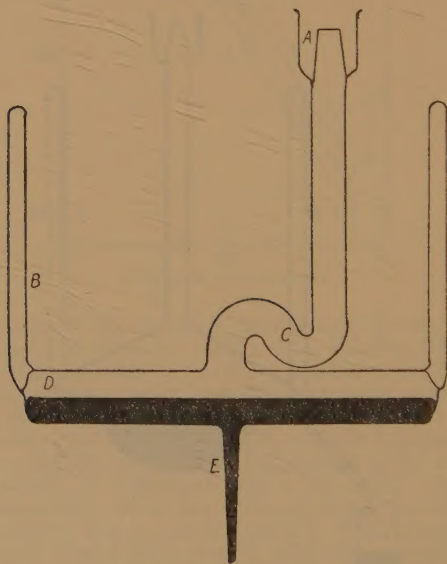
both heavy and light fractions are involved, then the value v varies as the sum of the cubes of ΔM . For example, seven months after Harkins and Broeker had attained an increase of 0.055 in the atomic weight of chlorine, Broensted and

* Harkins & Mann, unpublished work completed in 1922.

† Mulliken & Harkins, *J. Am. Chem. Soc.* xlv. p. 37 (1922); *'Science,'* liv. p. 359 (1921).

Hevesy obtained a minute increase of 0.006 unit and a decrease of 0.004 unit in the atomic weight of mercury. It is evident that this later separation had only about $1/600$ the value of that secured earlier by Harkins and Broecker. Since Broensted and Hevesy* gave no evidence that their mercury was pure, Mulliken and Harkins† evaporated mercury (fig. 3) at low pressures and condensed it by cooling with ice and water. This gave a separation of 0.027 unit and an efficiency of separation which was found to be 80 per cent. with one type of apparatus, and proved to be 5 per

Fig. 4.



Apparatus, similar to that of fig. 3, for the experimental determination of the coefficient of separation (B) of mercury into isotopes. The distance from the upper surface of the mercury to the upper condensing surface D is kept small. This surface is cooled by liquid air or solid carbon dioxide held by the Dewar jacket B. The value of B was found to be 0.0060.

cent. higher than that of Broensted and Hevesy. Thus the efficiencies proved to be of the same order of magnitude with ice water and with liquid air as cooling agents.

What was assumed to be an efficiency 100 per cent. was obtained by the use of a special evaporator, with the

* Broensted & Hevesy, 'Nature,' cvi. p. 144 (1920).

† *Loc. cit.*

evaporating and condensing surfaces close together, as given in fig. 4. The cooling was produced by solid carbon dioxide and toluene.

Table I. gives the change of atomic weight (ΔM) obtained in four later separations of mercury into isotopes, and includes the results obtained in the work of the present paper.

TABLE I.

Later Separations of the Isotopes of Mercury, with their Relative Values.

	+ M.	- M.	V +.	V -.	Value.
Broensted and Hevesy * ...	0.046	0.052	0.2 c.c.	0.2 c.c.	1.00
Harkins and Madorsky † ...	0.052	0.044	0.28	0.32	1.40
Mulliken ‡	0.0504	0.0512	22.00	22.00	121.00
Harkins and Mortimer	0.0962	0.0931	7.50	8.00	276.00

The *value* of the separation as given in the last column gives an estimate of the relative time necessary to produce the change of atomic weight obtained and the amount of material secured in the extreme fractions, that is, those which differ most in atomic weight. The relative value of the separations secured by Mulliken and by Harkins and Mortimer would be even higher if account were taken of the values of the intermediate fractions.

That large end fractions have a much greater value than those which are small may be illustrated as follows. The total separation obtained in the work described in this paper is 0.189 unit of atomic weight. However, the heaviest and lightest fractions contain about 100 grams each. By the use of a small unit of the general type described later, the atomic weight of the heaviest fraction could be increased by 0.022 unit in less than an hour, and by a few hours' work that of the light fraction could be decreased as much, so that in less than a day the total separation could easily be increased to 0.23 unit, and from the other heavy fractions this could in a few days be increased to more than 0.25 unit. This involves only the reduction of the volume of the end samples to about 0.2 c.c. That is, in the work of Broensted and Hevesy, and that of Harkins and Madorsky, the total separation attained would have been only about 0.05 unit of atomic weight if they had kept the samples as large as in

* Broensted & Hevesy, *Phil. Mag.* xliii. p. 31 (1922).

† Harkins & Madorsky, *J. Am. Chem. Soc.* xlv p. 591 (1923).

‡ Mulliken, *ibid.* p. 1592.

the present work. Their aim was to crowd all of the value in terms of change of atomic weight *alone* into the final fractions, which means that the work could not be continued farther in a systematic way; while in the present work the purpose has been to leave as uniform a set of fractions as possible over the whole interval, so that the progress of a later much greater separation may be continued without interruption.

The separation coefficient of zinc is about three and a half times that for mercury, so it would seem that it would prove a more satisfactory element to use if a rapid separation is desired. The attempts to separate the element into isotopic fractions have, however, given less favourable results. Thus Egerton and Lee* obtained values of $\Delta M = 0.017$ and $-\Delta M = 0.018$, while Harkins and Buckner† were able to increase the atomic weight by only 0.027 unit.

II. APPARATUS FOR THE RAPID SEPARATION OF MERCURY INTO ISOTOPIC FRACTIONS.

In the attempt to obtain an apparatus which would separate isotopic fractions of mercury very much more rapidly than in earlier work, Harkins and Madorsky developed the steel apparatus shown in fig. 5. The annular trough which holds the mercury is heated by a coil of nichrome wire, upon which it rests. Fig. 6 shows a similar, larger, apparatus in which the heating is secured by a coil of wire sheathed with steel, which lies at the bottom of the mercury. By the use of the smaller unit the separation of 0.1 unit at atomic weight, already mentioned, was obtained. The large unit was used only enough to prove that it gives a high efficiency with large amounts of mercury. In this apparatus a speed of evaporation of about 100 c.c. (more than 1 kg.) per hour gives an efficiency of 90 per cent. or more in the separation of isotopic fractions, if the pressure is kept between 0.001 and 0.0001 mm. of mercury.

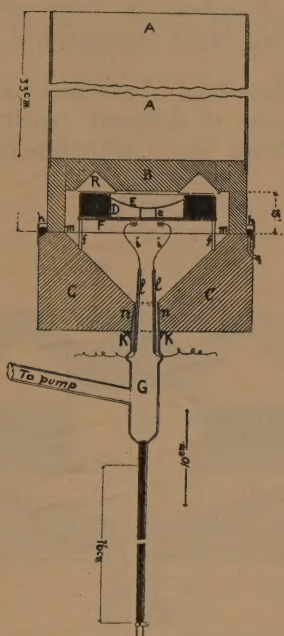
The light fraction of the mercury may be allowed to flow in a constant stream from the lower end of the glass tube at the bottom of the apparatus. This tube is bent at the bottom in such a way that it retains a column of mercury of barometric height, even if the stop-cock is kept open. This bend is not shown in the diagram. The mercury which flows from this tube is always about 0.004 unit of atomic weight lighter

* Egerton & Lee, Proc. Roy. Soc. ciii. A, p. 499 (1923).

† Harkins & Buckner, Unpublished work, begun in 1921 and completed in 1924.

than that present at the time in the trough. To prevent too much lag, this tube is made from a moderately narrow capillary.

Fig. 5.

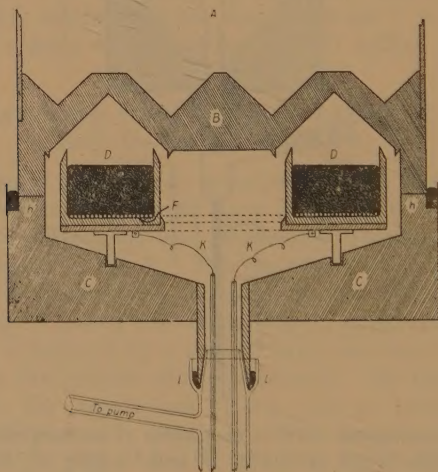


Steel vacuum apparatus for the separation of mercury into isotopes by vaporization at low pressures. B and C, parts of steel apparatus; h, mercury seal for vacuum; A, brass cylinder for ice and salt; D, annular steel trough of 190 c.c. capacity and 98 sq. cm. area of mercury surface; E, watch-glass with hole in centre for catching light fraction from inside eaves of condensing roof R. The mercury flows constantly into G, which ends below in a capillary tube of barometric height. This is bent at the bottom in such a way that mercury remains in the capillary with the stop-cock open. The heating coil F is directly underneath the trough D. In the newer models the platinum wires *ii* enter through insulating plugs through the steel base. The trough D is supported by glass rods *f*. When in operation the apparatus requires almost no attention, except for emptying the light fraction from the graduated cylinder in which it is collected about every half hour, and filling the cylinder with ice every two hours. The vacuum should be kept at about 0.0001 mm. of mercury. The apparatus has a small conical roof (not shown) at B which is used when it is desired to work with much smaller amounts of mercury. In this case a small circular trough is set on an independent heating unit in the centre of the apparatus, and the larger annular trough D is not used.

After this steel apparatus, with its attached mercury diffusion pump, backed by an oil-pump, is once set up, it is almost "fool proof," since it can be operated by a workman with almost no training. The only necessity is to keep the pressure in the apparatus sufficiently low while it is operating. With a battery of from six to twelve such units a comparatively rapid separation of the mercury may be secured.

The apparatus described above gives a separation of the mercury into samples of different density by a *diffusion* of atoms of mercury from liquid mercury, through the surface

Fig. 6.



Apparatus like fig. 5, except that the heating wires (F) are encased in steel and are in the mercury, but very close to the bottom of the trough. The area of the mercury exposed is also much larger.

of the liquid, which acts as a membrane with pores of molecular dimensions, into the gaseous phase above. If an efficiency of separation of 100 per cent. is to be attained, no atoms of mercury can be allowed to pass from the gaseous phase into the surface.

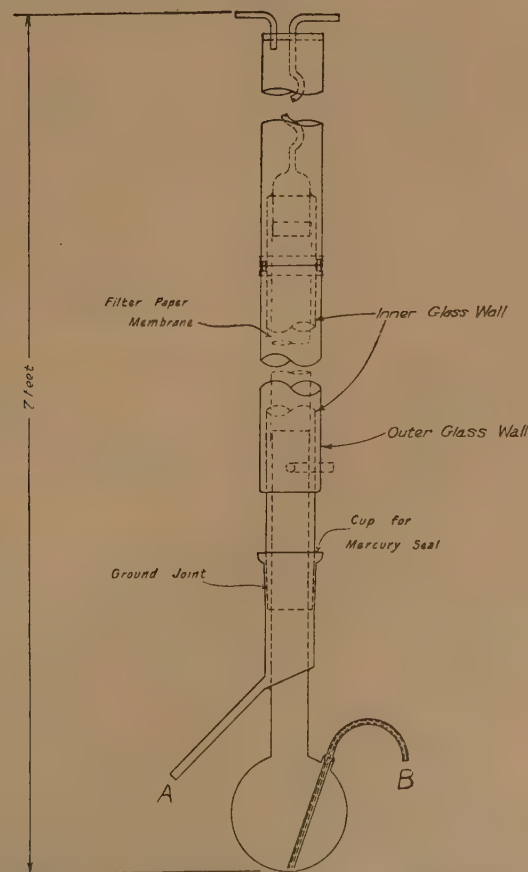
The great disadvantage of the method of evaporation at low pressures is that a considerable quantity of liquid must be used if a large area of surface is obtained, while in gaseous diffusion through a membrane a small amount of material may be diffused through a large area, which increases greatly the speed of the separation. The former method has the

additional disadvantage that a lower pressure is necessary for the same efficiency.

Combined Diffusion through a Membrane and Vaporization at Low Pressure.

In 1921 one of the writers (Harkins) constructed an apparatus which was intended to combine the separation of isotopic fractions by vaporization at low pressure with a

Fig. 7.



Apparatus for the separation of the isotopes of mercury by a combined evaporative-diffusion from the surface of mercury in the flask, and diffusion through a membrane of filter-paper. At B and A glass springs are sealed, and these lead into capillary tubes of barometric height filled with mercury. The complete unit is about 10 ft. high.

diffusion through a membrane, so that both processes might be brought about by one operation. Mercury vapour from a flask with a wide vertical neck was passed upward into a vertical tube of porous porcelain. The latter was surrounded by a double jacket of glass, between the walls of which cold water was caused to flow rapidly. The mercury condensed on the inner wall. The porcelain wall was found to possess certain disadvantages with respect to its use as a membrane. Its considerable thickness made the passage of the vapour comparatively slow. It was found, too, that if the porcelain tube was not heated by a heating coil of wire around it, mercury condensed near the outer surface, and this stopped the passage of the vapour.

An ideal membrane should be extremely thin and have extremely fine pores. The best membrane found in these respects is filter-paper (Whatman paper No. 5 was used), which, however, suffers from the great disadvantage that it is not durable. Nevertheless, six units with filter-paper tubes were built by Mulliken*, who in a few weeks of irregular operation obtained light and heavy fractions of 300 grams of mercury each, with a difference of atomic weight of 0.102 unit, an extremely large separation for so short a time.

The units used in our work were much more convenient than, though they were almost identical with, those used by Mulliken. The only important change was the substitution of a lower ground-glass joint (fig. 7) for a glass seal. This, however, reduced the time of changing the filter-paper in a single unit from 20 to 8 hours.

Six such units, set up on a single low bench and heated by extremely large Meker burners, were used. An asbestos-lined, well-ventilated iron hood, with a two-piece removable top, was fitted around each flask, in order to secure the uniformity of heating essential to keep the efficiency of the process constant.

III. THEORY OF THE SEPARATION OF ISOTOPES BY DIFFUSION.

In connexion with his work on the separation of the rare gases of the atmosphere, Lord Rayleigh† developed equations for the increase of density of the heavy fraction, or residue. These equations were put into a much simpler

* R. S. Mulliken, J. Am. Chem. Soc. xlv. p. 1592 (1923).

† Rayleigh, Phil. Mag. (5) xlii. p. 493 (1896).

form by Mulliken and Harkins *, who also developed relations for the change of density of the diffusate, that is, of the light fraction. Their general equation is

$$(1-k) \log C = k (\log (x_1)_0 - \log x_1) - \log (x_2)_0 + \log x_2. \quad (1)$$

A simpler equation,

$$\Delta M = \frac{(M_2 - M_1)^2 x_1 x_2}{cM} \ln C = D \ln C, \quad . \quad . \quad (2)$$

gives a good approximation. Here $k = c \sqrt{\frac{M_1}{M_2}}$, in which c is commonly assumed to be equal to 2, x_1 and x_2 are the mol fractions of the isotopes present, and M is the mean molecular weight. The increase of molecular weight for a certain cut varies as the square of the difference of the two molecular weights, and inversely as the mean molecular weight. A more accurate coefficient is designated as B , or

$$\Delta M = B \ln C. \quad . \quad . \quad . \quad (3)$$

For n identical operations the change of atomic weight of the diffusate (light fraction) is

$$\Delta M = -B \left(1 - BH \ln \frac{C}{C-1} \right) \ln \frac{C}{C-1}, \quad . \quad . \quad (4)$$

in which

$$B = \frac{(1-k) x_1 x_2 (M_2 - M_1)}{x_1 + k x_2} \quad . \quad . \quad . \quad (5)$$

and

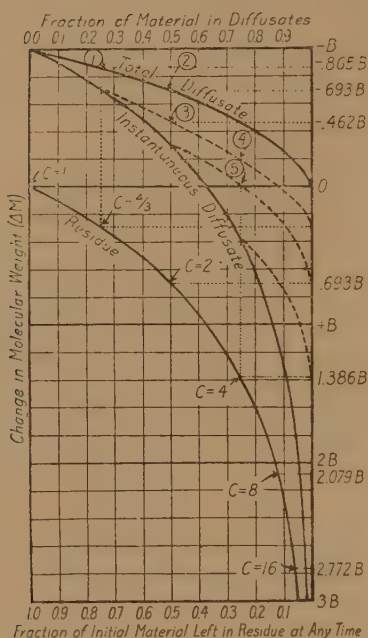
$$H = \frac{x_1 - x_2}{2x_1 x_2 (M_2 - M_1)} \quad . \quad . \quad . \quad (6)$$

The progress of a separation of isotopes up to a cut of 16 is shown in fig. 8. Equation (3) holds for any number of isotopes, but it is obvious that the expression for B is much more complicated than that given in equation (5). Fig. 9 shows the change of relative density of a number of isotopic materials as the cut progresses up to ten billion.

The above equation (3) shows the dependence of the atomic weight change on the separation coefficient B . In all known cases the coefficient B is small, which necessitates very rapid and systematically repeated operations if a large separation is to be obtained in a reasonable time. The efficiency of each individual operation is important, and is

* *Loc. cit.*

Fig. 8.

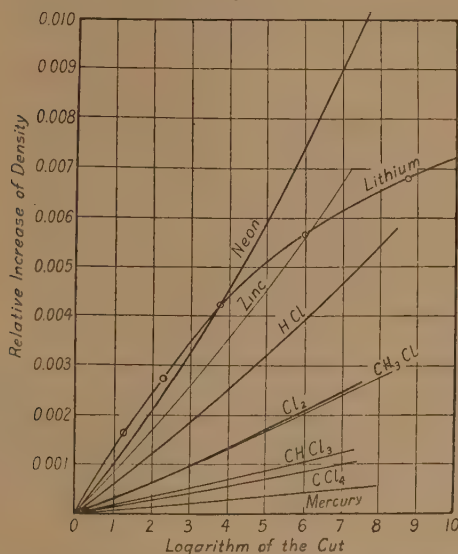


Generalized plot showing atomic or molecular weight of fractions obtained during a 100-per-cent. efficient diffusion or irreversible evaporation of a mixture of isotopes. The ordinates are expressed in terms of the "separation coefficient" B as a unit; this has a different numerical value (usually about 0.003 to 0.02) for each element. The value of B changes slightly with M . The symbol C stands for the "cut" or ratio of quantity of material in the residue at any time to the initial quantity; for any abscissa on the lower scale, the "cut" is merely the reciprocal quantity. The "instantaneous diffusate" curve gives at any point the composition of the material which is at any instant diffusing or evaporating from residual material corresponding to the same abscissa. Note that this curve has exactly the same form as the residue curve, and differs only in an upward displacement of the ordinates by B units. Each point on the "total diffusate" curve gives the average composition of the material which has diffused or evaporated from the beginning up to that point. The various dotted curves give the composition of fractions of the total diffusate beginning at various points after the beginning of the operation. The meaning of the total diffusate curves can be made clearer by a few examples. Thus, Point 1 gives the composition of the diffused or condensed fraction for the interval 0-25 per cent.; Point 2, for the interval 0-50 per cent.; 3, for 25-50 per cent.; 4, for 25-75 per cent.; 5, for 50-75 per cent. Taken in connexion with the residue curve, the total diffusate curves show how the original material can be divided efficiently into isotopic fractions. For example, the

curves show that the diffusate might be collected in fractions as follows: 0-25 per cent., $M = -0.865 B$; 25-50 per cent., $M = -0.462 B$; 50-75 per cent., $M = 0$. If the operation were stopped here, the residue would have the atomic or molecular weight $M + 1.386 B$, if M is the original atomic or molecular weight. The initial value of B is 0.0060 for mercury, 0.0095 for hydrogen chloride, 0.0049 for chlorine, about 0.002 for potassium, and 0.02 for zinc.

secured in the present apparatus by combining in successive steps two different methods of separation. The superposition of an efficient molecular diffusion on an inefficient evaporation accomplishes the effect of increased efficiency.

Fig. 9.



Relative increase of density $\frac{\Delta \rho}{\rho}$ with the logarithm of the cut.

The increase of molecular weight is equal to $\frac{M \cdot \Delta \rho}{\rho}$.

In any single diffusion the residue is enriched in the heavier isotopes, and the diffusate is enriched in the lighter isotopes. For the "instantaneous" diffusate the change in atomic weight (fig. 8) possible in this one operation is $\Delta M = -B$. Obviously, then, since B is small, large *decreases* of atomic weight can be secured only by repeated operations by subjecting the diffusate to many diffusions. With the residue on the other hand, large *increases* can be secured in a single operation by starting with sufficient

material and making a large cut. This is clearly shown by the equation which applies to the residue, $\Delta M = B \ln C$, in which ΔM depends directly on C , the cut. For an extended separation, however, regularly spaced intermediate fractions are vital, as a study of systematic fractionation will show, and so a compromise between the various attenuating factors must be sought. A cut of two is a good practical compromise for systematic fractionation. In this case

$$-\Delta M = +\Delta M = EB \ln 2 = 0.693 BE,$$

an equal and opposite change being effected in each operation. The efficiency of the process is then controlled largely by the diffusion rate, and by some artificial factors * whose effects have been very greatly minimized in the operation of the present apparatus.

IV. SYSTEMATIC FRACTIONATION.

Suppose a symmetrical fractionation procedure to be used for the division of an initially homogeneous sample into a set of fractions, all of some minimum size Q_0 , spaced at equal ΔM intervals on both sides of the initial composition M_0 . The simplest procedure † would consist of a series of individual operations, in each of which a fraction of size $2Q_0$ and composition M is divided into two fractions of size Q_0 and composition $M \pm EB \ln 2$. A study of the fractionation procedure shows that when the first $n-1$ pairs of fractions have already been produced, a total of n^2 additional unit operations will be required to produce the n th pair of fractions without permanently using up or increasing in size any of the previously-produced fractions. An example will help make this clear.

For simplicity consider the case where the inventory of the fractions of mercury is as follows:—

L3, L2, L1, zero mercury, H1, H2, H3 : each of size Q_0 . L with a suitable number following designates the light fractions, and H with a suitable number designates the

* Before the scheme of systematic fractionation was in effective use, efficiency was lost by combining fractions if they differed by less than six parts per million. In the later operation there was no need for this, since the fractions were regularly twenty parts per million from each other. The loss in efficiency occurring whenever a unit is emptied and refilled was minimized by shaking the unit so that very little mercury adhered to the condenser walls, and by adjusting the siphon so that the flask emptied completely.

† Mulliken, J. Am. Chem. Soc. xlv. p. 1601 (1923) gives essentially the same discussion.

heavy fractions ; thus L1 has been produced by one diffusion by a cut of two on ordinary mercury, and H2 has been produced from ordinary mercury by two cuts of two. It is desired to produce L4 and H4, and the theory indicates that n^2 or 4^2 additional unit operations will be necessary without permanently using up any of the previously-produced fractions.

The first step is to start with a volume of ordinary mercury of size $2Q_0$ and diffuse half of it at some previously determined rate so that the diffusate will have the composition L1 and the residue the composition H1. At this point the H1 is added, and the diffusion is continued. After a cut of two has been made on this mercury, the diffusate is ordinary mercury and the residue is H2. To this the H2 is added, and the process repeated. The diffusate is now H1 and the residue is H3. With the addition of the H3 and the final diffusion, the diffusate has the composition H2 and the residue has the composition H4, provided none of the previously-mentioned causes of low efficiency was operative. These four operations have produced the H4, but have used up the H3.

The same procedure is carried out with the light mercury, with this difference : between each diffusion the unit must be emptied and refilled, thus consuming at least 50 per cent. more time to carry out the same number of operations. Since the L1 was produced at the same time as the H1, only three operations are necessary to produce the L4. By these seven distinct diffusions we have produced L4 and H4, but have used up L3 and H3, so that the inventory would be :

L4...L2, L1, zero, H1, H2, ...H4.

Applying the same reasoning to the production of L3 and H3 shows that five distinct diffusions are necessary ; to supply the L2 and H2 used up in this last process, only three diffusions are required ; and, lastly, an additional diffusion replaces the L1 and H1 used to produce L2 and H2. The inventory would now be :

L4, L3, L2, L1, zero, H1, H2, H3, H4 ;

and the total number of operations required to produce the L4 and H4 without using up any of the intermediate fractions is $7+5+3+1=16$, or 4^2 as the theory indicated. The total volume of mercury diffused in producing this n th pair of fractions is $Q=Q_0 \times 2^n$. Thus, if Q_0 is 50 c.c., as in this case, Q equals 800 c.c.

The corresponding time expended in producing the n th pair is evidently

$$t_n = n^2 \frac{(Q_0)}{(D)}, \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

where D is the rate of production of the light fraction. Now

$$\Delta M = \pm nEB \ln 2, \quad . \quad . \quad . \quad . \quad . \quad (II.)$$

so that

$$t_n = \frac{(\Delta M)^2 Q_0}{E^2 B^2 (\ln 2)^2 D} \quad . \quad . \quad . \quad . \quad . \quad (III.)$$

The time required to produce a pair of extreme fractions is thus proportional to the *square* of the difference between its composition and that of the original raw material, and *inversely* proportional to the squares of the efficiency and of the separation coefficient. Since, in the production of extreme fractions, intermediate fractions of some minimum size must be maintained, the time of production of any extreme fraction should be taken to include the total time of production of all intermediate fractions.

$$t = t_1 + t_2 + \dots + t_n = (1^2 + 2^2 + 3^2 \dots + n^2) Q_0/D$$

or

$$t = \frac{n(n+1)(2n+1)}{6} \frac{Q_0}{D} \quad . \quad . \quad . \quad . \quad . \quad (IV.)$$

This equation can be used to calculate the *operating time** required to obtain any given fraction of composition ΔM , if the corresponding value of n is calculated from equation (II.). The *actual* working time required will be about *three* times this, because of the considerable time needed for repair and replacement of units, of loss of time when the units are not in operation together, of time required in starting and stopping the apparatus and in emptying and refilling units, and because of low efficiency when the air-pressure suddenly increases, thus changing the diffusion rate.

For $n=1$, t has the value $n^3 Q_0/D$; for $n=5$, t has the value $0.44 n^3 Q_0/D$; for $n=10$, $t=0.385 Q_0/D$; and for $n=\infty$, $t=n^3 Q_0/D$. Approximately, then, t is proportional to n^3 , except for the smallest values of n . We had above, $\Delta M = \pm nEB \ln 2$ (equation (II.)), giving for t

$$t = \frac{K (\Delta M)^3 Q_0}{D E^3 B^3} \quad . \quad . \quad . \quad . \quad . \quad (V.)$$

* Actually, it is much simpler to calculate the time by dividing the total volume which must be diffused by D , and then making the allowances suggested.

Equation (V.) shows the rapidly mounting difficulty of increasing ΔM , even by systematic fractionation; it shows the great effect of the value of B , the separation coefficient, on the possibility of obtaining a large difference in atomic weight in a moderate time; also B varies with ΔM , and there is a slight progressive decrease in the separation as it approaches completion. This shows the importance of using a method and apparatus which can deal with small intermediate fractions (Q_0), yet operate at high speed (D). Also, for a given $\Delta M/B$, t is a *minimum* if DE^3/Q_0 is a *maximum*.

V. ACTUAL FRACTIONATION SCHEME EMPLOYED *.

Because the systematic fractionation scheme on a cut of 2 had not yet been put into effective operation when this research was undertaken, considerable time was consumed in getting the fractions regularly spaced, once the efficiencies for various rates had been determined. The change in composition for diffusate and residue for a cut of two was determined for rates of 30 c.c. per hour, 40 c.c., 50 c.c., 60 c.c., and 70 c.c. per hour. At 30 c.c. per hour the rate of production of the light fraction is much too slow; at 70 c.c. per hour the life of the membrane is considerably shortened, offsetting the increased rate of production †. The practical compromise in this case was a rate of diffusion of 50 cc. (680 g.) per unit per hour on a cut of 2, in which the change in atomic weight between diffusate and residue is 0.008 unit; that is, the diffusate is 0.004 unit lighter and the residue is 0.004 unit heavier than the original material. Substitution of this value in the equation $\Delta M = 0.693 EB$ gives an efficiency of 92 per cent. This method of systematic fractionation requires a minimum number of fractions, and eliminates entirely calculations of composition.

A set of sixteen heavy fractions differing from each other by 0.004 unit of atomic weight, and a set of fifteen light fractions the same interval apart, were secured after much

* The mercury produced by Mulliken, total difference of atomic weight equal to 0.102 unit, was used in this work. The writers had cooperated in its production. The separation already attained corresponded to 12 heavy and 11 light fractions. This was increased to 25 light and 25 heavy fractions. However, many of the original 23 fractions had been used up, so much work was done in getting a complete set of these initial fractions.

† To renew a membrane takes eight hours.

diffusion, and combination of fractions less than 0.002 unit apart. At this stage the inventory was noted :

Heavy Fractions.			Light Fractions.		
c.c.			c.c.		
2550		H1	884		L1
559		H2	354		L2
199		H3	510		L3
100		H4	60		L4
108		H5	210		L5
196		H6	152		L6
49		H7	100		L7
47		H8	100		L8
49		H9	149		L9
50		H10	50		L10
54		H11	51		L11
52		H12	54		L12
47		H13	50		L13
51		H14	50		L14
54		H15	55		L15
47		H16			

The object now was to achieve the largest possible separation with this material most efficiently, that is, with the expenditure of the least time. Recourse was had to a critical detailed study of this phase of systemic fractionation. The schemes actually employed on the light and heavy side are shown in full in figs. 10 and 11. These will help to illustrate the general procedure, and will serve to clarify the important considerations.

Sunier* has shown, in his careful study of this process, that there are three factors of prime importance: (1) the starting-point; (2) the number of rows worked; and (3) the ratio of the number of cubic centimetres diffused to the number of cubic centimetres yield of the end fraction†. In general the analysis of the first two rows is an accurate guide to determine the starting-point. This was done for a number of distinct starting-points.

The first case considered was that of H2 as the starting-point for the final diffusions on the heavy side. For the

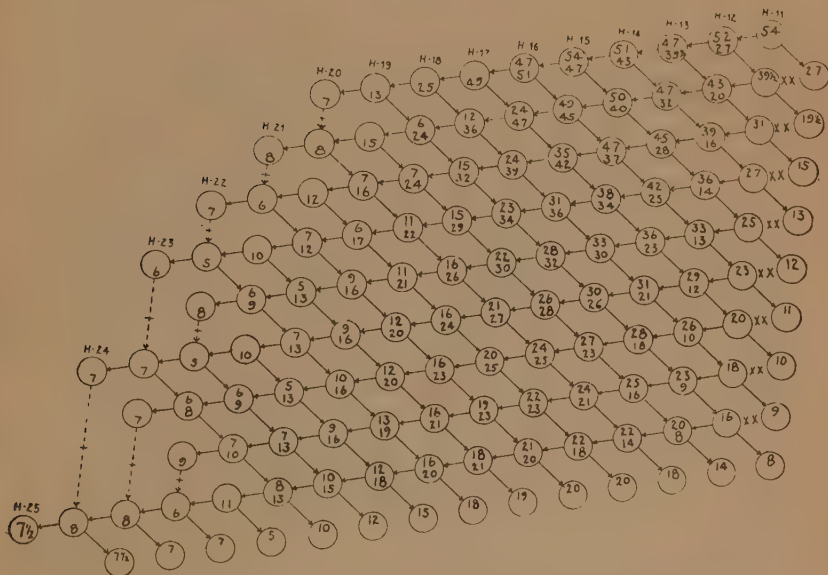
* Sunier, Doctor's Dissertation, Univ. of Chicago, Dec. 1927.

† In these final diffusions a small 200 c.c. flask was used instead of the 500 c.c. one, and it was safe to run the residue down as low as 5 c.c. (see p. 619).

first row worked, the number of cubic centimetres diffused is 1646 and the yield is 7 c.c., the ratio of 1646 to 7 being very high. For the second row the volume diffused drops to 1356 c.c. and the yield rises to 7.75 c.c., but the ratio is still too high.

The next case examined was H8. The intermediate starting-points were rejected upon application of the preliminary test, which is as follows: to produce H20 from H6, for instance, requires 20-6, or 14 cuts of 2 on H6. The

Fig. 10.



Actual fractionation scheme used on the heavy fraction.

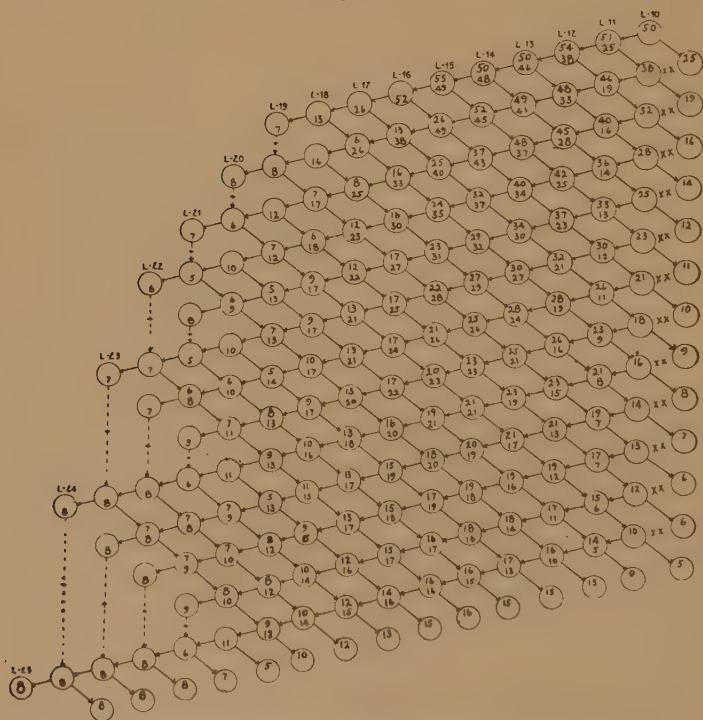
yield of H20 from H6 only in this process would be given by initial volume of H6

$$\frac{1}{2^{14}}$$

, a very small quantity. Of course, much of the material is reworked into the scheme, so that the test is not a rigorous one, but it can be used safely as a first approximation. For H8 the figures are for the first row 432/7 and for the second row 399/7.75, a considerable decrease in the volume diffused with no diminution in the yield. By elimination of other starting-points, H11 was

decided upon as the most practical and satisfactory from every point of view. In this case the ratio for the first row is 297.5 to 7, and for the second row the ratio is 262.5 to 8. In all the cases considered more material is produced in the second row than in the first row. These considerations bring out clearly the value of working more than one row.

Fig. 11.



Actual fractionation scheme used on the light fraction.

A similar examination was made of the light fraction. By a similar process of reasoning and calculating, L10 was chosen as the most practical starting-point. Before the final diffusions were begun, the densities of the starting fractions were checked to provide a means of determining just what loss of efficiency is experienced in working with small volumes. This factor was balanced somewhat by a lower diffusion rate which tends to increase the efficiency.

VI. DISCUSSION OF THE FRACTIONATION SCHEME EMPLOYED.

A. *The Heavy Fraction.*

The inventory of the heavy fractions used was :

c.c.	
54	 H11
52	 H12
47	 H13
51	 H14
54	 H15
47	 H16

These volumes appear as the figures in the upper part of the first six circles of the first row. The lower figure in the circle is the volume of mercury resulting from the previous diffusion. The directed arrows show where the products of each diffusion go. (The broken arrows at the end of the rows indicate the addition of mercury of identical composition before another diffusion is carried out.) Consider H12 in the first row. When half of the 54 c.c. of H11 has been diffused, the residue, 27 c.c., has the same composition as the 52 c.c. of H12. This latter volume is then added to the flask, and the diffusion is continued. Thus in any circle the upper figure represents the stock on hand, and the lower figure represents the volume resulting from the previous diffusion. The diffusion of H12 gives 39.5 c.c. of H13 as residue, and 39.5 c.c. of H11 as diffusate. The stock of H13 is added to the flask, and the process of diffusion on a cut of two is continued down through the entire row. It is understood, of course, that with the heavy fraction the process is continuous, that is, that no emptying of the unit is required between diffusions.

The 39.5 c.c. of H11 is introduced into the flask of a second unit, and the second row of this fractionation scheme is started only one diffusion behind row one. In this manner the mercury is used as quickly as it is produced. After the first row has been worked completely, the second row is only a step behind, so that the 7 c.c. of H20 which had been produced in row 1 is added to the H20 produced on the completion of row 2, and the diffusion is carried one step beyond, yielding H21. This general procedure is carried out throughout the entire fractionation, as many rows as possible being worked simultaneously.

The completion of nine full rows yielded 7.5 c.c. of H25 and the following fractions:—

c.c.		c.c.	
7.5	H23	18	H16
7	H22	19	H15
7	H21	20	H14
5	H20	20	H13
10	H19	18	H12
12	H18	14	H11
15	H17	124.5	H10

In addition there is the complete inventory of fractions from H9 down to ordinary mercury which was left untouched in this scheme.

B. *The Light Fraction.*

Very much more work was required to achieve the same relative separation of the light fraction, because of the more frequent emptyings and refillings necessary. To minimize the time spent in doing this, the order of progress of the fractionation scheme was modified.

The light fractions used were:

c.c.	
50	L10
51	L11
54	L12
50	L13
50	L14
55	L15

The first operation of the first row consists in diffusing half of the 50 c.c. of L10, obtaining 25 c.c. of L11 and 25 c.c. of L9. The flask is then emptied as nearly completely of L9 as possible, and all of the L11, 76 c.c., is introduced*. Two diffusions are carried out on this fraction before the flask need be emptied. The first of these yields 38 c.c. of L12 as diffusate, and 38 c.c. of L10 as

* This mixing of unlike fractions is unavoidable. The quantity remaining behind in the flask and adhering to the condenser walls is very small, yet its effect is to lower the efficiency of the process sufficiently to tell on the density. Every precaution, short of using a new apparatus for each set of diffusions, was exercised to minimize this loss of efficiency.

residue. Another cut of two is made on the residue, after which the flask is emptied. By these two diffusions the second operation of the first row and the first operation of the second row of the fractionation scheme are consummated without emptying the unit. In the meantime the L12 had been introduced into another unit and the diffusion started, so that this unit uses the material which the first unit is producing. Thus the application of the fractionation scheme to the light fraction was down and backward, instead of out and forward, as on the heavy side. Essentially the progress of the light fraction is the same as the progress of the heavy, although more time is consumed, especially at either end of the scheme. This is due to the many more emptyings and refillings demanded.

The completion of thirteen full rows yielded 8 c.c. of L25 and the following fractions :--

c.c.		c.c.	
8	 L23	15	 L15
8	 L22	16	 L14
8	 L21	15	 L13
7	 L20	15	 L12
5	 L19	13	 L11
10	 L18	9	 L10
12	 L17	148	 L9
13	 L16		

In addition there is the complete set of fractions from L8 down to ordinary mercury which this scheme does not embrace.

VII. THE DENSITY DETERMINATIONS.

The mercury used had been purified by prolonged agitation with nitric acid, followed by 5 distillations in a current of air at low pressure according to the method of Hulett and Minchin*, who claim that a single distillation gives a completely pure product. The first and last portions were rejected in each distillation, and a final distillation *in vacuo* was made.

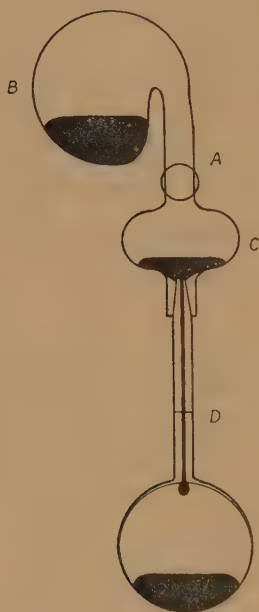
Before the final density determinations were made on L25 and H25, they were further purified. Two additional distillations, by the method indicated above, were carried out, and

* Hulett & Minchin, Phys. Rev. xxi. p. 388 (1905).

the middle portion from the second distillation was collected separately for the density determination*.

The pycnometer used was a small one, patterned after that devised by Harkins and Mulliken (fig. 12). The filling

Fig. 12.



Pycnometer.—The mercury is put into the bulb B; the pycnometer D is then put in place. The apparatus is evacuated by means of a mercury condensation pump. The mercury is moved in B by rotating the apparatus around the side-tube A, which connects with the vacuum-pump by means of a ground-glass joint. When a very low pressure has been attained the mercury is spilled over into C. Air is then admitted through A, and the bulb and stem of the pycnometer are filled completely with mercury. The pycnometer is then put in a thermostat at a temperature slightly above 25° . Later it is put into a thermostat at $25^{\circ}000$, and the meniscus comes almost exactly to the fine mark at D. This is caused by the choice of just the proper temperature higher than 25° . The small deviation from the mark is determined by a cathetometer. By this means the relative density may be easily determined to one part in two million in the larger of the pycnometers used: in the smaller to better than 3 parts in a million.

* Additional evidence for the purity of this mercury is furnished by Dr. F. A. Jenkins, who recently completed an accurate study of the spectra of samples I116, I125, L15, and L20, the results of which are as yet unpublished. In a private communication he has informed the

device was slightly modified by the introduction of a ground joint, to allow greater ease in handling and filling the pycnometer. By filling it at a low temperature, and then allowing the mercury to overflow at a suitable temperature, calculated previously from the dimensions of the pycnometer and the coefficient of expansion of mercury, the meniscus would come approximately to the mark at 25°·000 C. Its distance from the mark was then measured by means of a travelling microscope fitted with a telescope objective, and the observed weight of the filled pycnometer is corrected accordingly. The pycnometer held 17·67110 grams of ordinary mercury. The details of the density determinations and the precautions observed are essentially those given in full by Mulliken and Harkins*.

Results of the Density Determinations.

Weight of pycnometer + dish	Average.....	14·25046
Weight of pycnometer + ordinary mercury + dish	1st	31·92155
	2nd	31·92152
	3rd	31·92158
	Average.....	31·92155
Weight of mercury		17·67110

Determinations of Density of H25.

	Weight of pycnometer + H25 + dish.	Weight of H25.	Atomic weight change.
1st determination (corrected)	31·93000	17·67955	+0·0959
2nd " " "	31·93005	17·67960	+0·0964
3rd " " "	31·93004	17·67959	+0·0963
4th " " "	31·93001	17·67956	+0·0960
5th " " "	31·93001	17·67956	+0·0960
		Average	+0·0962

From this the atomic weight of H25 is 200·706.

writers that in all his work, using various methods of exciting the spectrum, no lines other than those of mercury were ever recorded. We may regard this as a searching confirmation of the absence of metallic impurities, especially in the heaviest fraction, where even a slight impurity of the original mercury would be expected to accumulate.

* *Loc. cit*

Determinations of Density of L25.

		Weight of pycnometer + L25 + dish.	Weight of L25.	Atomic weight change.
1st determination (corrected)		31.91338	17.66293	-0.0927
2nd " " " "		31.91335	17.66290	-0.0931
3rd " " " "		31.91334	17.66289	-0.0932
4th " " " "		31.91333	17.66288	-0.0933
5th " " " "		31.91335	17.66290	-0.0931
Average				-0.0931

The atomic weight of this L25 is 200.517.

Discussion and Results.

There has been obtained 7.5 c.c., or 101.96 grams of H25 of atomic weight 200.706, an increase of 0.0962 unit. The efficiency of these final diffusions with the smaller volumes is only slightly less than that which was obtained with larger quantities. On the basis of the previously-determined efficiency of 92 per cent., the theoretical change in atomic weight would have been, for H25, 0.100 unit. The actual operative efficiency was 88 per cent. That is, in these last 14 cuts of 2, the residue, in each cut, became heavier by only 0.0038 unit, instead of 0.004 unit, a difference which is within the limits of accuracy of the density determinations. Of course, with the heavy fraction there is some *favourable* mixing of unlike fractions. For example, on completion of the first row of the fractionation scheme the flask is emptied of H20, and H11 is introduced to start another row. This mixing is very favourable, and doubtless served to reduce the loss of efficiency, even though the quantity of H20 which remains behind is very slight (see footnote, p. 616).

For the heavy fraction 8 c.c., or 108.76 grams, of L25 of atomic weight 200.517 has been obtained, with a decrease of 0.0931 unit of atomic weight. The unavoidable mixing of unlike fractions, unfavourable in this case, is reflected in the lowered efficiency. Although a smaller flask was used throughout all the latter work, this factor was not enough in itself to maintain the efficiency of the evaporation and diffusion. The theoretical change in atomic weight would have been 0.100 unit, but was only 0.0931 unit, an efficiency of 85.6 per cent. To be sure, the slower diffusion rate operative with the smaller fractions contributed somewhat to maintain the efficiency determined for larger volumes.

The existence of appreciable quantities of mercury of densities different from ordinary mercury under the same conditions offers opportunities for the investigation of the variation of properties with isotopic composition.

The lightest and heaviest fractions of the mercury ($\Delta M = 0.189$) were used by Dr. F. A. Jenkins* for the study of the wave-lengths of the lines $\lambda\lambda 5461, 4359, 4078,$ and 4047 . The intensities of the satellites were also compared. No differences were detected by the use of the 8-inch plane grating in the fifth order, or by the 30-plate Michelson echelon. Specimens of isotopic mercury have been given to the Bureau of Standards for the determination of their electrical conductance.

With isotopic chlorine ($\Delta M = +\Delta M = 0.055, -\Delta M = 0.04$) Dr. Jenkins found a shift in the direction of higher frequency for the heavy fraction. This is in accord with what was found for lead by Harkins and Aronberg†, and later by Merton‡. However, the *relative* difference in the atomic weights of the isotopic chlorine used was about three times that for the mercury, which may account for the difference in the results of the spectroscopic investigations.

Dr. Jenkins has calculated for us the change in composition of the mercury attained in the end fractions of our separation on the basis of a total change of 0.18 unit of atomic weight, which is slightly *less* than that actually obtained. The results of these calculations are given below. Recently Aston§ has succeeded in resolving the components of the mass-spectrum group of mercury, and gives the following atomic weights, with a rough estimate of the proportions:—

198 (4) 199 (5) 200 (7) 201 (3) 202 (10) 204 (2).

Assuming that the bracketed numbers represent approximately the relative numbers of atoms of each isotope, we can calculate the change in these values corresponding to a given change in atomic weight. For the best samples of mercury used in this investigation, the atomic weight differed by more than 0.18 unit. In the fractional diffusion by which these were produced the material was always cut in half, one of the resulting fractions serving as the material for the succeeding diffusion. This operation was repeated 25 times for the "heavy" fraction (atomic weight

* Jenkins, Phys. Rev. xxix. p. 54 (1927).

† Harkins & Aronberg, Proc. Nat. Acad. Sci. iii. p. 710 (1917).

‡ Merton, Proc. Roy. Soc. A, c. p. 84 (1921).

§ 'Nature,' cxvi. p. 208 (1925).

change $+0.1$), and 20 times for the "light" fraction (atomic weight change -0.08). For each of the final fractions we may apply the theoretical equations of Mulliken and Harkins * to determine the change in average molecular weight, and in relative quantity, of any pair of isotopes. Five suitably chosen pairs give a complete solution and the new isotopic composition. In obtaining the values of Table II., pairs were chosen such that the average molecular weight of each was as near as possible to that of ordinary mercury, since these decrease in amount during the fractionation at almost exactly the same rate as the total quantity of mercury. Allowance was also made for the change in the rate of separation as it progresses, since this becomes appreciable in the relatively large changes brought about for the lightest and heaviest isotopes.

TABLE II.

Isotope	198.	199.	200.	201.	202.	204.
Initial percentage	12.90	16.13	22.58	9.68	32.26	6.45
Percentage in light fraction...	14.09	17.01	23.00	9.52	30.65	5.73
Percentage in heavy fraction .	11.51	15.03	21.96	9.83	34.23	7.45

The absolute values are, of course, not as accurate as the table indicates, but are given merely to show the relative changes. The latter we may assume to be qualitatively correct, and indicate changes of 27 and 20 per cent., respectively, of the initial proportions of isotopes 204 and 198.

VIII. SUMMARY.

(1) A comprehensive survey of the separation of isotopes actually achieved has been made, and the possibilities of any larger separations have been discussed. The difference of atomic weight between samples of mercury as obtained in this work is 0.189 unit, the largest difference in atomic weight yet achieved by artificial means.

(2) The apparatus developed by Harkins and Mulliken was modified by the introduction of a ground joint between the flask and condenser, which greatly reduced the time of repair and replacement of the filter-paper membrane.

(3) The theory of isotopic resolution by evaporation and diffusion is briefly reviewed. It is shown that the change in atomic weight, ΔM , depends largely on the separation coefficient, the cut, and the efficiency.

* Journ. Am. Chem. Soc. lxiv. pp. 47, 51 (1922).

(4) The details of the method of systematic fractionation, with cuts of 2, used in this work, are given in detail. The time required for the production of any extreme fraction, allowing for the time necessary to build up the intermediate fractions, is given by $t = K(\Delta M)^3 Q_0 / DE^3 B^3$, in which K is a constant, B the separation coefficient, E the efficiency, and D the rate of production of the light fraction. Study of this equation shows the difficulty of obtaining large values of ΔM , especially if B is small, as it is with mercury.

(5) The completion of nine full rows of the fractionation scheme applied to the heavy fraction yielded 101.96 grams of H25, 0.0962 unit of atomic weight heavier than ordinary mercury, and a set of 23 fractions each 0.004 unit heavier progressively than ordinary mercury. The completion of thirteen full rows of the fractionation scheme applied to the light fraction yielded 108.76 grams of mercury 0.0931 unit lighter than the ordinary element; in addition there is the corresponding set of 23 fractions, each progressively 0.004 unit lighter than ordinary mercury.

(6) The existence of this isotopic mercury affords an opportunity for the investigation of the variation of properties with isotopic composition.

University of Chicago,
April 9, 1928.

LVIII. *The Relation between Kinematic Pairs and Links in a Mechanism.* By WILLIAM J. WALKER, D.Sc., Ph.D.,
University of the Witwatersrand, Johannesburg *.

THE usual discussion in treatises and text-books on kinematics of machinery regarding the relationship between the number of pairs and number of links in a mechanism leads to the formula

$$L = 2P - 4, \dots \dots \dots (1)$$

where L is number of links and P number of pairs.

This formula, which is based upon a somewhat arbitrary elimination of certain pairs in any mechanism, necessitates, for complicated mechanisms especially, a careful tabulation of all pairs and elements, in order to arrive at the correct

* Communicated by the Author.

number of pairs P in the mechanism to be inserted in formula (1). In other words, P in that formula does not represent the actual number of pairs in a mechanism. Clearly, therefore, a formula involving P as the actual number of pairs in any mechanism, a number easy to compute without tabulation, is a desirable feature in any system of machine analysis. The following investigation of this problem leads to such a formula, and will be found to fit the link-pair relationship for any definite mechanism, however complicated.

In every case the building-up of connected chains in a mechanism consists in the addition of three turning pairs and two links for every additional quadric chain after the first. It might appear at first sight that three extra links are required, but since one of these must be a fixed link, this may be considered as embodied in the fixed link of the first or primary chain. Hence the P series for all mechanisms is

$$P=4, 7, 10, 13, \dots \text{etc.},$$

the general member of which is given by

$$P=4+3(n-1),$$

where n equals number of quadric chains. Similarly, the link series is given by

$$L=4, 6, 8, 10, \dots \text{etc.},$$

the general member of which is

$$L=4+2(n-1).$$

Eliminating n between these two equations for P and L gives

$$L = \frac{2P+4}{3} \dots \dots \dots (2)$$

The only point to be borne in mind when applying this formula is that when a number of links l furnish elements at a common point of conjunction, the number of pairs at such point of conjunction should be $l-1$. This follows naturally from the fact that one of the l links may be considered to furnish one common element, completing the pairs for the remaining $l-1$ elements.

With this strictly logical observance, formula (2) will be found of general applicability to all mechanisms.

LIX. *The Photoelectric Properties of Thin Films of the Alkali Metals.* By N. R. CAMPBELL. (Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley.)

SUMMARY.

THE thin films mainly studied are those produced by depositing an alkali metal on some other material, driving it off by heat, and subjecting the remaining film to a discharge in hydrogen. By this process photoelectric cathodes can be produced that have very remarkable and stable sensitivity to red light; photoelectric currents can be obtained with light of $\lambda 8000 \text{ \AA}$ of the same order as those obtained in normal potassium cells with light of $\lambda 4500 \text{ \AA}$. The sensitivity depends very greatly on the material on which the film is deposited.

The observations are closely related to those of Ives on the photoelectric properties of thin films and to those of the many workers who have investigated the effects of gas films on photoelectric emission. The surfaces concerned almost certainly consist of a succession of monomolecular layers, similar to those of caesium and oxygen on tungsten (Langmuir and Kingdon) or of barium and oxygen or other gases (Ryde). But the conditions of their formation are exceedingly complex, and little progress has been made towards an analysis of their constitution.

The observations seem to have an important bearing upon attempts to correlate thermionic and photoelectric emission.

(1) *Origin of the Experiments.*

THE accidental interchange of the connexions of a gas-filled potassium photoelectric cell led to the observation that the photoelectric threshold of the anode lay much further towards the red end of the spectrum than that of the cathode. The area of the anode was much less than that of the cathode, yet, when the cell was exposed to diffused light through a red screen, the emission from the small electrode was greater than that from the large. It appeared at once that if the large electrode could be made as sensitive to red light as the small, the resulting cell would be very useful,

for it would make photoelectric measurements as easy at the red end of the spectrum as at the blue end.

Further inquiry showed that the difference between the two electrodes (it has been found in almost all the gas-filled cells from various sources that have been examined) arises primarily from the thickness of the layer of potassium covering them. The large electrode is covered with a massive layer, the smaller with a thin film acquired by condensation of the vapour at room temperature. The difference arising from this cause is reinforced by the passage of a discharge in hydrogen according to the Elster-Geitel sensitizing process, which doubtless has the effect (among others) of producing a gas film on the surface. Accordingly the study of the remarkable red sensitivity of the anodes of normal cells would naturally follow paths that have been partially explored by previous workers. For Ives* has studied the photoelectric properties of thin films and shown that their threshold may lie further towards the red than that of the massive material; and many workers† have shown that the removal of gas films may transfer the threshold towards the blue, and consequently that the formation of suitable layers may transfer it towards the red. Unfortunately, however, I have been unable so far to relate these observations closely to those of others and thereby to explain them; the facts that will be set forth are at present practically useful rather than theoretically significant. Accordingly it will be better to describe them as part of a completely unknown field rather than as particular illustrations of established principles.

(2) *The First Experiments.*

All the earlier experiments were made in cells of a normal type shown in *Phil. Mag.* iii. p. 947, fig. 1*b* (1927). The photoelectrically active layer is deposited on the metallic coating of a shallow cup forming the bottom of the cell, which is the cathode; a nickel gauze parallel to it serves as anode. It may possibly be relevant to record that the cells were made of borosilicate glass with molybdenum leading-in wires. During, or after, manufacture the cells could be exposed to the light from a tungsten source at about 2700° K. with the interposition of screens. The screens

* H. E. Ives, *Astrophys. J.* lx. p. 209 (1924).

† The latest are H. Klumb, *Zeit. J. Phys.* xlvii. p. 652 (1928); R. Fleischer, *Ann. d. Phys.* lxxxii. p. 75 (1927).

were those of the Wratten monochromatic series, usually No. 70, which transmits wave-lengths longer than λ 6400 Å, and No. 75, which transmits wave-lengths between λ 5400 Å and λ 4550 Å. The photoelectric current was measured by a galvanometer.

A typical experiment consisted of three or four stages each leading to a different state of the cathode. After the cell had been evacuated for an hour at 400° C., the active metal, usually potassium, was distilled into it; no elaborate precautions were taken to ensure chemical purity. The metal was deposited on the metallic coating by heating the remainder of the cell by a flame. The cathode thus covered with a thick layer of the active metal is in state A. Sometimes hydrogen was introduced at this point and the metal sensitized by the discharge; the sensitized state of the thick layer is A'. In the next stage the thick layer is driven from the cathode by the application of a small flame and deposited on the walls; a window for the entrance of the light is preserved at the top of the cell by warming it. When the thick layer evaporates from the cathode a marked change in appearance spreads over its surface; the end of the evaporation can therefore be determined sharply. The cathode is now left covered with a very thin film, such as Ives studied, which is quite invisible. If the cell is left to cool, further distillation of the potassium is apt to occur, and a visible layer may be formed again on the cathode or may obscure the window. Accordingly it is convenient to introduce hydrogen to a pressure of about 1 mm. as soon as the layer has been driven from the cathode; the gas equalizes temperatures within the cell and directs condensation to the upper portion; the window, if obscured, can be cleared again without deposition of the metal on the cathode. The cathode is now in state B. Last, the thin layer is sensitized by passing a discharge of a few milliamperes through the hydrogen with the cathode of the cell as the cathode of the discharge. The cell is now in state B'.

The photoelectric current excited by the light incident on the cell through the two screens was measured in each state. If gas was present, allowance was made for absorption of the electrons or ionization by collision, so that the numerals given, termed for brevity the red sensitivity and the blue sensitivity, are proportional to the photoelectric emission under the red and blue light. Since comparisons between the sensitivities in the various states alone are in question, no useful purpose would be served by reducing

the readings further; they are given in scale divisions. The following table gives some typical results:—

TABLE I.

State.	Blue sensitivity.	Red sensitivity.
A (thick layer)	70	< 1
A' (thick layer sensitized)	480	3
B (thin layer)	400	23
B' (thin layer sensitized)	450	600

(3) *The Conditions of Red Sensitivity.*

The features to which attention should be directed are these. The sensitization of the thick layer produces an increase of the red sensitivity as well as of the blue; in fact the ratio of the sensitivity in A' to the sensitivity in A is greater for the red than for the blue. The substitution of the very thin film for the thick layer reduces slightly the blue sensitivity, but increases the red; the blue sensitivity is still, however, far the greater. Sensitization of the thin film changes the blue sensitivity little, but produces an enormous increase in the red sensitivity.

If the experiment is repeated, either on another similar cell or by driving the potassium again to the cathode of the same cell and repeating the cycle, these features will recur. But the values of all the sensitivities may differ by factors as large as 2. It has been found impossible to obtain quantitative consistency, however great the precautions taken to repeat the conditions, and therefore the effects of changes in the procedure cannot be established certainly unless they are large. Nevertheless, some conclusions concerning the various states can be established.

Little need be said about states A and A', for they are well known. The blue sensitivity in state A can be increased by repeated distillation of the active metal, but no appreciable red sensitivity can be induced even when the greatest care is taken to secure chemical purity. During the passage of the discharge which produces state A' both sensitivities rise to a maximum and then fall. This maximum seems independent of the pressure of the gas or the current carried by the discharge. In general it increases with the sensitivity in the preceding state A, but the correlation is not perfect. The red sensitivity in A' is more variable than the blue.

State B is presumably the nearest approximation in these experiments to the state studied by Ives (*loc. cit.*); the sensitivity may therefore be expected to change with the time since the thin layer was formed. Some variation of the nature described by Ives is usually found, but the changes that I have observed are much smaller than his. A steady state is reached in about half an hour after the thick film is driven off; all statements refer to this steady state. The sensitivities in this state are very variable, but no connexion could be found with the procedure employed in producing it. They do not seem to depend directly on the temperature to which the cathode is heated (so long as it is sufficient to drive off the film and insufficient to soften the glass), or on the time for which the temperature is maintained, or on the presence of hydrogen while the cathode cools.

In state B' there is also sometimes an initial variation with the time since the cessation of the discharge, leading to a final steady state. (Such variations are also found in state A'.) It generally consists in a fall of both sensitivities and of the ratio of the red to the blue, but sometimes it is wholly absent. The nature and the duration of the discharge may have a marked influence on the final sensitivity, but their influence is very complex. Any discharge produces some increase in red sensitivity; the occurrence of any visible glow for a second will produce a marked effect; it is not necessary even that the surface to be sensitized should be the cathode; some sensitization will be produced if it is the anode. Further, in some circumstances a discharge of whatever nature, enduring only for a few seconds, will produce the full sensitivity of state B', which is unaffected by further passage of the discharge; the circumstances in which sensitization is thus independent of the nature of the discharge are, in general, those in which the greatest red sensitivity is attained. In other circumstances the red sensitivity depends greatly on the duration and the direction of the discharge; the sensitivity produced will now be greater if the active metal is the cathode of the discharge than if it is the anode, and there will be an optimum time of discharge that gives the greatest sensitivity, but this time will vary very greatly in different experiments.

States A and A', being those of thick layers of the active metal, are independent of the material on which the layer is deposited (as might be expected), except in so far as it may influence the purity of the metal. But states B and B' depend very greatly on this material. The results given in

Table I. (p. 636) were obtained when the underlying material of the cathode was silver, deposited chemically; experiments were also made with platinum, deposited from a platinizing solution, and with copper electroplated on silver. With platinum both the blue and red sensitivities and the ratio of the red to the blue are somewhat smaller than with silver; with copper the blue sensitivity is smaller but the red sensitivity very much greater. Lesser variations of the same kind can be produced by treatments that might be expected to change the surface composition of the cathode, although its main bulk is unaffected. Thus, if potassium is distilled repeatedly from a silver cathode, the red sensitivity in states B and B' will be reduced; at the same time, as has been noted, the blue sensitivity in state A and both the blue and red sensitivities in state A' will be somewhat increased. This treatment might be expected to remove electronegative impurities (*e.g.* oxygen) from the surface. On the other hand, if oxygen is admitted to the cell and then removed, the red sensitivity is likely to be increased. Similar changes in platinum are not so easily produced. They can be produced in copper, but not so regularly; again, oxidation of the surface seems favourable to red sensitivity, reduction unfavourable. The greatest red sensitivities were obtained when the copper was deliberately oxidized in air before the cell was pumped.

The nature of the active metal is, of course, also important, but here the relations are not those that might have been anticipated. In states A and A' the red sensitivity of caesium is much greater than that of potassium, but this is by no means true of states B and B'. The difference between states A and A', on the one hand, and states B and B' on the other, is much greater with sodium and potassium than with caesium and rubidium, and so is the difference between state A and state A' or between state B and state B', produced by sensitization. The greatest red sensitivities have been obtained with potassium on copper; sodium in state B' on copper gives as great a red sensitivity as any that I have been able to produce with caesium in any circumstances. The sensitivities, both red and blue, of caesium in state B' are so small that it is not certain that they are due to caesium rather than to traces of other alkali metals present as impurities.

Table II. summarizes some of the more important results. The three columns of figures give the photoelectric emission from various cells when similarly exposed to the light from the same tungsten source at 2700° K. through the red and

blue screens and without any screen at all. The first part of the table refers to the various alkali metals prepared in the normal manner, the cathode being covered with thick layers sensitized in hydrogen (state A'); the second part refers to various cathodes in state B'. Each cell is a favourable specimen of its class, but never the most sensitive that has been prepared.

TABLE II.

Cell.	No filter.	Photoelectric Emission.	
		Red filter ($\lambda > 6400 \text{ \AA}$).	Blue filter ($\lambda 5400\text{--}4550 \text{ \AA}$).
State A'.			
Sodium.....	2150	<0.2	40
Potassium.....	6300	<0.2	255
Rubidium.....	2250	0.4	126
Cæsium.....	830	3.7	21
State B'.			
Potassium on silver.....	950	42	23
Sodium on copper	735	14	17
Potassium on copper ...	2050	328	31
Rubidium " ...	700	21	20
Cæsium " ...	76	7	1.5

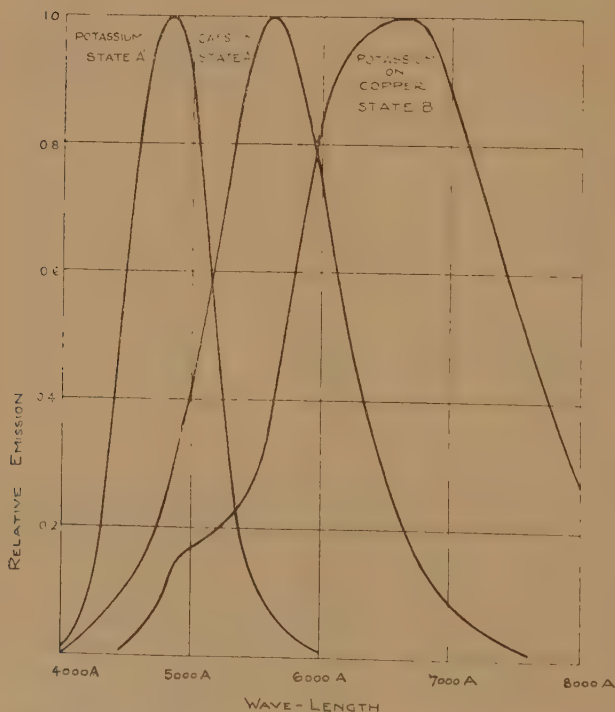
The table suggests that if maximum sensitivity throughout the whole range of the visible spectrum is required, a combination of the normal potassium cell (state A') and a potassium-on-copper cell (state B') should be used. Closer inquiry confirms this suggestion. No cell has been found which is more sensitive than both of these two at any part of the spectrum; cæsium cells, generally said to have their maximum sensitivity in the yellow, are not more sensitive than the potassium-on-copper cells even in this region.

(4) *Relation between Frequency and Sensitivity.*

So far the results have been stated in terms of the purely empirical magnitudes, red and blue sensitivities, depending upon the particular source and screen employed. For theoretical purposes they should be expressed by the relation between the frequency and the ratio of the photoelectric emission to the energy of (or possibly to the number of quanta in) the incident light. Some measurements have been made with spectrally resolved light from a source of

known energy distribution, but I do not propose at present to report them. For some unexpected difficulties have appeared, and the examination of the results of other workers on the alkali metals in states A and A' reveals serious discrepancies; it is of no use to publish further discrepant measurements unless the reason for the discrepancy can be made clear.

Fig. 1.



The Photo-Electric Properties of Thin Films of the Alkali Metals.

But it may be useful to give a few results which, while still empirical, are rather more complete. In fig. 1 the emission excited by the light issuing from the slit of a certain monochromator is plotted against the nominal wave-length. Each abscissa corresponds to light of the same quality in each curve, but the ordinate scale is different for each curve, unit emission for each curve being taken to be that for the nominal wave-length that gives maximum

emission. Curves are given for potassium and caesium in state A' and for potassium-on-copper in state B'.

It will be seen that there is every evidence that the increase in red sensitivity characteristic of the change from state A' to state B' represents a shift of the threshold towards the longer wave-lengths and not a mere change in the ratio of finite sensitivities. If a curve for potassium-on-silver in state B' were added, it would appear again that the threshold depends on the underlying material as well as on the active metal. In the curve for potassium-on-copper there are signs of an irregularity in the neighbourhood of $\lambda 5000 \text{ \AA}$; this may be compared with the double maxima shown in similar experiments by Richardson and Young on oxidized potassium sensitized by the hydrogen discharge *. But the irregularity is not so great as they found and it does not always appear; it probably indicates that the surface is not homogeneous.

(5) *A Practical Difficulty.*

It appears, then, that the potassium-on-copper cell is likely to be of great practical utility, but it has one drawback that must be mentioned. It cannot be filled with argon or other rare gas and used as a gas-filled cell, because the presence of these gases, and still more the passage of a discharge through them, destroys the red sensitivity †. On the other hand, they can be filled with hydrogen, and it is possible to obtain as great magnifications by ionization by collision in hydrogen as in argon, though they are less stable. But, as Elster and Geitel found long ago, the hydrogen gradually disappears; this was their original reason for using an inactive gas rather than hydrogen. The difficulty can be overcome partially by attaching a palladium tube to the cell through which hydrogen can be added, but this is not wholly convenient. The absorption of hydrogen is being investigated and some more convenient solution may be found. It displays some remarkable features; thus the absorption is much more rapid and persistent when the potassium is deposited on copper than when it is deposited on silver. But this matter must be left over for the present.

* O. W. Richardson & G. F. A. Young, Proc. Roy. Soc. A. cvii. p. 386 (1925).

† I have never seen a record of the fact, but many users of photo-electric cells must know that a similar change occurs with potassium in state A'. In an ordinary argon-filled cell, standing unused for some time, the blue sensitivity decreases while a red sensitivity develops. The passage of a discharge through the cell for a few seconds increases the blue sensitivity, but very greatly decreases the red sensitivity.

(6) *Second Series of Experiments.*

When it was clear that surface gas films were playing a large part in the process it became desirable to make experiments in conditions such that the films could be removed or controlled by the usual high vacuum technique. Accordingly cells were constructed in which the cathode consisted of a plate, well separated from the walls, which could be heated by radiation or by electronic bombardment from a tungsten filament placed behind it; the anode was again a parallel nickel gauze. The following materials were used as cathodes, each in a different cell: carbon, aluminium, iron, nickel, cobalt, copper, zinc, molybdenum, silver, tungsten, platinum, gold. In the first experiments with such cells the cathode was freed from gas as far as possible by heating before the first deposition of the active metal. State B was then produced by driving off the active metal with gentle heat, and state B' by the discharge. Potassium was used exclusively as the active metal.

To my surprise and disappointment, the development of red sensitivity proved more and not less complex, less and not more controllable, in these cells than in the type used at the outset. Moreover there were some outstanding differences between the two series of experiments. The variations of the sensitivity with the time were now much larger; in state B they were in accordance with those to be expected from the work of Ives. As the plate cooled, both blue and red sensitivities rose to a maximum and then declined; the changes in the red sensitivity were much greater than those in the blue; the maximum ratio of red to blue sensitivity occurred at about the same time as the maximum of either. Ives seems to have investigated these changes only for one metal, platinum; his comparisons of different metals refer only to the state finally attained; my experiments suggest that if he had followed the earlier stages he would have found far more difference between the various metals in the stage of maximum sensitivity than he found in the final stage. As regards the final stage my results concerning the difference between the various metals are not wholly in accordance with those of Ives, but then I have not been able to obtain complete consistency in different experiments. Ives does not say if he experienced any difficulty in repeating his results quantitatively.

In state B' similar changes occur, but more slowly. The maximum red sensitivities observed with silver, copper, and platinum (the metals common to the two series) were of the same order as those found in the simple cells, but these

high red sensitivities were never permanent. Both blue and red sensitivities, and the ratio of the red to the blue, decayed; finally they were not always higher than those obtainable in the final stage of state B.

Again the effects of the discharge were far more complex. Sometimes the state was attained in which any discharge would produce almost immediately the full red sensitivity, but now sometimes the discharge would actually decrease, instead of increasing, both the red sensitivity and the blue. An apparently exact repetition of the same experiment would sometimes produce qualitatively different results. With the molybdenum cathode the passage from B to B' was often produced by the mere presence of hydrogen; the red sensitivity increased greatly as soon as the gas was introduced, and no further increase could be produced by the discharge. Indications of sensitization by hydrogen without the discharge were observed with other metals, but in none so markedly.

Attempts to reproduce the old results were made by admitting oxygen and other gases to the plate, in the hope of forming a suitable gas film on it. The addition of oxygen, especially to some metals, increased the red sensitivity obtainable in the consequent following states B and B', but it did not make the sensitivity permanent or the effects of the discharge less complex and inconsistent. Permanency could only be attained by avoiding from the outset all attempts to free the plates from gas and by following as nearly as possible the procedure used in the simple type of cell.

(7) Results of Second Series.

In spite of all these irregularities regular differences between different materials for the cathode could be established. For instance, if they are compared on the basis of the maximum red sensitivity occurring in state B' at some time after the discharge, and if the greatest value obtained for this maximum in a series of experiments is taken, then it appears that the order of this red sensitivity is somewhat as follows: copper, zinc—cobalt, nickel—gold, molybdenum, silver, platinum—iron, tungsten, aluminium, carbon. Here the cathode is supposed to have been freed from gas as completely as possible by heating before the deposition of the potassium. It is highly improbable that all surface films were removed in all cases; thus aluminium cannot be freed from surface oxide by bombardment, zinc evaporates at a temperature certainly too low to remove gas from other

metals, and it is well known that it is almost impossible to remove the gas absorbed in the interior of copper. Indeed it is possible that from no metal was the gas perfectly removed, for the conditions were not ideal.

If, on the other hand, no attempt is made to remove surface gas, if the cell is simply baked, leaving the cathode covered, in some cases, with a visible layer of oxide, then the order is rather different. Thus iron comes up into the third group and gold into the second, but copper and zinc are still better than all others.

Some subsidiary observations may be added which may be relevant when explanation is sought. When the potassium was first distilled into the cell a visible layer would often form on every part of it except the cathode; the anode gauze would be covered by a brilliant metallic layer, while the neighbouring cathode remained unaffected. The cathode cannot have failed to condense the vapour because, being thermally insulated, it became hot, for the anode is equally insulated and of smaller thermal capacity. But if the potassium were distilled repeatedly from one part of the cell to another, with intervals of cooling (in order that the cathode might remain cool), the metal would always finally condense on the cathode. The reason for this behaviour must be doubtless sought in the work of Knudsen and his successors, and in particular of Cockerft *, who has shown that the critical temperature for the condensation of vapours upon imperfectly clean surfaces is particularly high. For when the vapour refused to condense there was always reason to believe that the cathode was not clean, and, once it had condensed, it would always condense again readily.

When there was difficulty in condensing the vapour on the cathode it always displayed some photoelectric sensitivity before the visible layer of the active metal appeared. But in no case was the red sensitivity thus developed before full condensation as great as that developed after condensation and subsequent evaporation. Ives (*loc. cit.*) records no difference † between the properties of films formed by slow condensation and those formed by removing a thick film; probably there is no difference if the surface on which condensation occurs is clean, but there certainly may be a difference if it is not.

* J. D. Cockerft, Proc. Roy. Soc. A, cxix. p. 293 (1928).

† Except with gold, which is permanently altered in appearance by the deposition of the active metal. My observations here agree entirely with his.

A few attempts were made to determine whether the temperature at which the visible layer of potassium disappears from the cathode was independent of the material on which the layer is deposited. The measurements were very rough, but they disclosed no great variation between different materials. It should be recorded that state B' is always destroyed, at least partially, by heating the cathode to the temperature at which the passage from A to B occurred; that is to say, state B persists at temperatures at which state B' is unstable.

(8) *Some Theoretical Considerations.*

The main object of this paper is to draw attention to a large class of interesting and practically important facts requiring further investigation. But a brief mention of some of the more obvious theoretical conclusions that they suggest may be desirable.

There can be no doubt about the general nature of states B and B'. The surface of the cathode in these states is compounded of the actual metal, the underlying material, hydrogen, and some other substances (of which oxygen is probably one) in such a manner that the photoelectric properties of the compound surface are affected by all these constituents, but that its work function may be less than that of any of them. A few years ago a suggestion that such a compound surface consisted of patches might have been plausible, but to-day it is certainly more plausible to suggest that it consists of a succession of monomolecular layers and is similar to the surfaces compounded of caesium, tungsten, and oxygen studied by Langmuir and his associates* or to those more complicated surfaces, in which barium is an element, that Ryde† has studied so exhaustively. Of course, neither Ives's experiments nor my own provide any evidence as cogent as that provided by these workers that the layers are truly monomolecular, but the onus of proof would seem to rest on anyone who would maintain that there is not an essential similarity.

Nevertheless there are differences, the chief of which is the far greater irregularity of my observations. The explanation may possibly lie in less perfect experimental conditions;

* I. Langmuir, *Phys. Rev.* xxi. p. 380 (1923); I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. A*, cvii. p. 61 (1925).

† J. W. Ryde. Paper not yet published. Ryde had reached his main conclusions before the beginning of these experiments, which were very greatly influenced by his work.

I may not have avoided sufficiently the presence of disturbing substances. But it must be remembered that my most regular results were obtained in the conditions apparently least perfect, namely in the simple cells from which the observations started. It is more likely that the difference lies in the conditions of temperature; all thermionic measurements are made at temperatures that destroy or modify profoundly the photoelectric sensitivity; the peculiarly variable surfaces that are studied here may not exist at all at these temperatures. Further, the surface compounded of monomolecular layers may be in a state of dynamical rather than statical equilibrium; interchange of material between the cathode and its surroundings may be proceeding constantly. In thermionic experiments the cathode is always hotter than the walls, in photoelectric experiments it is at the same temperature. The state of the photoelectric cathode may be influenced to a greater degree than the thermionic by variations in the state of the walls, which are very difficult to control; indeed some evidence, though it is not so far conclusive, has been obtained of a correlation between the state of the walls and the sensitivity of the cathode. Again, if the equilibrium is dynamical, the small sensitivity of caesium in state B' may be explained; the vapour-pressure of the metal may be so high that very few molecules are present on the surface at any one time. These questions must obviously be examined by experiments at different temperatures.

Concerning the exact nature or the order of succession of the monomolecular layers little can be suggested at present. Oxygen is almost certainly a constituent of some at least of the surfaces, and in state B' hydrogen ions are almost certainly another. For since normally any kind of discharge in hydrogen will produce an increase in red sensitivity, while the mere presence of hydrogen will not, the conclusion is almost inevitable that the primary function of the discharge in sensitization is the provision of hydrogen ions. Measurements have been made recently on sensitization by means of the Townsend discharge, supported by photoelectric emission from the cathode, in which the number and energy of the ions can be controlled and ascertained. The results are not very easy to analyse and, once more, will be reserved for the present, but they are consistent with the view that the change from state B to state B' is intimately connected with the arrival of hydrogen ions at the cathode. The irregular effects of the discharge are probably due to changes, other than mere ionization, that it produces; thus it may heat the

cathode or sputter material from the cathode and deposit it on the walls, or from the walls and deposit it on the cathode.

According to this view states A and A', the unsensitized and sensitized states of thick layers, must be essentially similar to states B and B'; the only difference is that in states A and A' the material of the underlying cathode is the same as that of one of the superimposed monomolecular layers. The remarkable observations of Richardson and Young (*loc. cit.*), in which they obtained great red sensitivities and a threshold in the infra-red by subjecting an oxidized potassium surface to the hydrogen discharge, are essentially similar to my own; they probably realized a state B' of potassium on potassium. The threshold that they observed was not that of potassium; that is to say, it was not that of a cathode consisting uniformly of potassium from a homogeneous interior to a boundary at which the electrons are emitted free to move under small external fields. Such a cathode is obtainable, if at all, only when the most strenuous endeavours are made to free the surface from gas; the observations of Fleischer* suggest that its threshold lies well towards the blue end of the spectrum.

These remarks are relevant when attempts are made to relate the thermionic and photoelectric properties of such metals as potassium. It is clearly very difficult to ensure that the two properties studied experimentally are those of the same surface. But a more general consideration concerning the relation of thermionics and photoelectricity may be offered; it was suggested to me in conversation by Mr. R. H. Fowler. The difference between the thermionic emission from different substances is often regarded as determined wholly by the work function. But another property must enter, namely, the emission coefficient; that is to say, the ratio between the number of electrons acquiring energy greater than the work function to the number emerging from the surface during any period. If the cathode is completely homogeneous the neglect of the emission coefficient may be justified. For then the surface will probably consist electrically of a simple rapid change of potential, all in one direction; if the emission coefficient varies from one metal to another, its variation is likely to be correlated closely with that of the work function. But if the cathode is not homogeneous, if there are several superimposed monomolecular layers at its surface, this correlation may be absent, for the work function is determined by the total change of potential through the whole series of layers,

* R. Fleischer, *loc. cit.*

while the emission coefficient may well be determined by the manner in which the change occurs. The potential may have maxima and minima within the series of layers, and these are likely to effect the emission coefficient, though they may not affect the work function.

In photoelectric emission the work function corresponds, of course, to the threshold; the emission coefficient is probably represented by the sensitivity for frequencies considerably greater than that of the threshold. In my experiments the work function is determined roughly by the red sensitivity, the emission coefficient by the blue sensitivity. Table II. (p. 639) shows that the two sensitivities are not at all closely correlated; it is not true, even in the most general way, that the cathode with the lower frequency for its threshold has the greater emission for higher frequencies; indeed, if films of the same active metal on different cathode materials are compared, the converse of this proposition is more nearly true. The mutual independence of red and blue sensitivities accords well with the theory that the surfaces are composed of successive layers; it shows also that any relation between the variation of the thermionic emission with the temperature and the variation of photoelectric emission with the frequency is likely to be far more complicated than is indicated by any of the theories that have been proposed hitherto.

LX. *Chemical Interactions corresponding to the Constant of Mass Action being a Function of the Volume and Masses of the Constituents as well as of the Temperature, and Catalytic Action.*—II. By R. D. KLEEMAN, B.A., D.Sc.*

§ 1. *Introductory Remarks.*

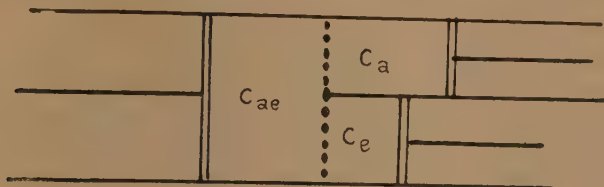
IN a previous paper† the writer has investigated some of the conditions under which the constant of mass action is a function of the volume of the gaseous interacting mixture and the masses of the constituents, as well as of the temperature. This paper is a continuation of the investigation. The reader should acquaint himself with the matter in the paper quoted.

The investigations in question are based on differential equations obtained by means of a certain isothermal cycle

* Communicated by the Author.

† Phil. Mag. vi. pp. 195-203 (1928).

which may be varied somewhat depending on the given conditions. The cycle usually involves a chamber containing the reacting gaseous mixture, separated from a number of other chambers by membranes, each of which is permeable to one of the constituents. If this number is two the apparatus has the form shown diagrammatically in the figure.



§ 2. *The Effect of Small Dissociation on the Constant of Mass Action of a Gaseous Mixture.*

Suppose that a mixture of M_a mols of molecules a and M_e mols of molecules e at the pressure p is contained in the chamber C_{ae} of the apparatus shown in the figure, whose volume is v . The chambers C_a and C_e are separated from the chamber C_{ae} by membranes permeable to molecules a and e respectively, the pressures in these chambers will accordingly be denoted by p_a and p_e , and the corresponding volumes of mols of molecules a and e by v_a and v_e respectively. The differential equation of the reaction with respect to the volume v as independent variable is *

$$v \frac{\partial p}{\partial v} - M_a v_a \frac{\partial p_a}{\partial v} - M_e v_e \frac{\partial p_e}{\partial v} = 0. \quad (1)$$

Let us suppose that the pressure of the free molecules a in the mixture is extremely small. The equation of state of the molecules a in the chamber C_a is then *not* given by

$$p_a v_a = RT, \quad (2)$$

where T denotes the absolute temperature, but by †

$$p_a v_a = \xi_a RT, \quad (3)$$

where ξ_a is a function of v_a and T , or

$$\xi_a = \phi_0(v_a, T). \quad (4)$$

ξ_a differs very little from unity except when v_a is very large, being then less than unity. For the molecules in the chamber C_{ae} , whose concentration is not small, ξ may be

* Phil. Mag. v. pp. 620-629 (1928).

† Phil. Mag. v. pp. 1191-1198 (1928).

taken equal to unity. It will now be evident from a previous investigation * of the solution of the differential equation (1) that K the constant of mass action is now obtained a function of v , even if we suppose that the other free molecules obey the orthodox gas law.

Similarly, it can be shown by means of the differential equation †

$$v \frac{\partial p}{\partial M_a} - M_a v_a \frac{\partial p_a}{\partial M_a} - M_e v_e \frac{\partial p_e}{\partial M_a} = 0 \quad . \quad . \quad (5)$$

of the reaction, in which M_a is the independent variable, that the constant of mass action is a function of M_a , and so on.

A similar result can be shown to hold for other reactions in which the concentration of one or more of the constituents is very small.

Let us, for example, consider the reaction between equal numbers of mols of molecules a and e ,



in which the concentrations of the free molecules a and e are extremely small.

The equation (29) in a previous paper ‡ can now easily be shown to have the form

$$\frac{\partial C_a}{\partial v} = \left(\frac{M_a}{v} \right) \frac{C_a}{C_a v - 2M_a \xi_a}, \quad . \quad . \quad . \quad . \quad (7)$$

supposing that $\xi_e = \xi_a$, and taking into account that $v_a = \xi_a / C_a$, where C_a denotes the concentration of the molecules a in the chamber C_{ae} §. If this equation is solved and the expression obtained for C_a substituted in the equation

$$K \left(\frac{M_a}{v} - C_a \right) = C_a^2, \quad . \quad . \quad . \quad . \quad (8)$$

also given in the paper quoted, the functional form of K in respect to v is obtained.

Since the constant of mass action can be determined only from concentration measurements, and it is difficult to measure small partial concentrations, it will be difficult to prove this result and others of the same kind experimentally.

* Phil. Mag. v. pp. 621-622 (1928).

† *Loc. cit.*

‡ Phil. Mag. v. pp. 626-627 (1928).

§ The gas equation (2) applies to the molecules a in the chamber C_{ae} since the total molecular concentration is not small, while the gas equation (3) applies to the molecules a in the chamber C_a . Since the pressure of these molecules is the same in the two chambers (otherwise diffusion from one chamber to the other would take place), it follows that $v_a = \xi_a / C_a$.

The constant of mass action under these conditions, it will be recognized, is very small. In a previous paper* the writer showed that the constant of mass action is approximately a function of the temperature only when the dissociation is small. The result is based on the supposition that equation (2) holds exactly. Since this is not the case the quoted result must be modified somewhat accordingly.

§ 3. *The Catalytic Effect of a Surface Absorbing Substance on the Constant of Mass Action of a Reaction.*

Let us suppose that the surface of the walls of the cylinder of the chamber C_a absorbs some of the gaseous molecules a in contact with it till a point of saturation is reached. This absorption we will suppose consists simply of the deposition of a layer of molecules on the surface which can be removed by mechanical means, such as passing another solid substance over the surface. The mass of molecules a deposited per cm.² is a function of the pressure p_a of the molecules and the temperature, and it may therefore be written $\phi(T, p_a)$. The total mass M_a' absorbed is therefore equal to

$$M_a' = A \cdot \phi(T, p_a), \quad . \quad . \quad . \quad . \quad (9)$$

where A denotes the area of the exposed surface of the cylinder.

Let us next suppose that the mixture of molecules a and e in the chamber C_{ae} is passed through the first of the two cycles described in a previous paper†. The process (a) of this cycle consists in passing the mixture into the chambers C_a and C_e at constant pressures, during which the external work

$$M_a'' v_a p_a + M_e v_e p_e - p v$$

is done, where M_a'' denotes the mass of molecules a in the chamber C_a at the end of the process, which are not deposited on the chamber walls. In the process (b) the chambers C_a and C_e are increased in volume by a small amount, during which the work

$$M_a'' p_a \cdot \partial v_a + p_a v_a \cdot \partial M_a'' + M_e p_e \partial v_e$$

is done, where M_a'' must be considered a variable since it depends on A and p_a . In the process (c) the substances a and e are returned to the chamber C_{ae} at constant pressures, giving rise to the external work

$$-(M_a'' v_a p_a + M_e v_e p_e - p v) - \partial(M_a'' v_a p_a + M_e v_e p_e - p v),$$

* Phil. Mag. v. pp. 263-271 (1928).

† Phil. Mag. v. pp. 620-629 (1928).

where M_a'' , as before, must be considered a variable. The deposited molecules a are shaved off during the process by the piston of the chamber C_a . In the last process (d) the volume of the mixture is decreased by ∂v , giving rise to the external work

$$-p \cdot \partial v.$$

On equating to zero the total external work done, we obtain the equation

$$v \frac{\partial p}{\partial v} - M_a'' v_a \frac{\partial p_a}{\partial v} - M_e v_e \frac{\partial p_e}{\partial v} = 0, \quad . \quad . \quad (10)$$

which has the same form as the equation (1) obtained in the paper quoted, where M_a^* is replaced by M_a'' . Now

$$M_a'' = M_a - M_a' = M_a - A \cdot \phi(T, p_a) \quad . \quad . \quad (11)$$

by equation (9). Hence equation (10) be written

$$v \frac{\partial p}{\partial v} - \{M_a - A \cdot \phi(T, p_a)\} v_a \frac{\partial p_a}{\partial v} - M_e v_e \frac{\partial p_e}{\partial v}. \quad (12)^*$$

The other equations which are used with this equation to obtain a solution, which are given in the paper quoted, do not contain $A \cdot \phi(T, p_a)$, since when the mixture is completely in the chamber C_{ae} no molecules a are deposited on a surface. It follows, therefore, from the investigation in this paper that the solution of (12) will give K a function of v , M_a , and M_e , as well as of T , whose form with respect to v is determinate. The form with respect to M_a and M_e is determined by two equations given by the second cycle, which may be obtained from equation (12) on substituting ∂M_a and ∂M_e in succession for ∂v . *Thus a solid substance which condenses a gaseous substance on to its surface has a catalytic effect on the constant of mass action of a reaction involving the gaseous substance.*

The expression for K will also involve A . This signifies that a continual deposition and evaporation of molecules a in the chamber C_a takes place during which they undergo a process of activation at the surface, which changes their chemical behaviour. This activation of the molecules when not in contact with the surface will gradually disappear. Hence the average extent of activation of a mass of gaseous molecules will depend on the area A of the activating surface. This result is the theoretical explanation of the

* If the deposition is supposed to take place on the surface of the chamber C_{ae} and we suppose that the mass $A \cdot \phi(T, p_a)$ is deposited while the mass M_a is in the gaseous state, the corresponding differential equation, as can easily be shown, is obtained from equation (12) on changing the sign of the term $A \cdot \phi(T, p_a)$

result observed long ago that the activity of a catalytic agent depends largely on the area of the exposed surface.

§ 4. *The Catalytic Effect of a Bulk Absorbing Substance on the Constant of Mass Action.*

Let us suppose, as was done in a previous paper*, that the walls of the chamber C_a are permeable to molecules c which are contained in an adjacent reservoir of infinite dimensions. The presence of the molecules c may affect the nature of the molecules formed from the molecules a in the chamber, especially if the molecules c are in a dense or liquid state. It is well known that dissociation or polymerization of the molecules of a gas absorbed by a liquid or solid may take place. The osmotic pressure $p_{a'}$ of the molecules a in the chamber C_a is under these conditions equal to αp_a , where p_a is the pressure in the chamber C_{ae} , and α is a quantity which may be greater or less than unity. α is evidently a function of p_a and T , and we may therefore write

$$p_{a'} = p_a \alpha = p_a \cdot \psi_1(T, p_a). \quad . \quad . \quad (13)$$

The volume $v_{a'}$ of a mol of the molecules a in the chamber C_a may be written

$$v_{a'} = \psi_2(v_a), \quad . \quad . \quad . \quad (14)$$

where v_a is the volume when the molecules c are absent.

If the mixture is passed through the first of the cycles described in a previous paper†, the same differential equation in form as before is obtained, where $p_{a'}$ and $v_{a'}$ take the place of p_a and v_a , or

$$v \frac{\partial p}{\partial v} - M_a v_{a'} \frac{\partial p_{a'}}{\partial v} - M_e v_e \frac{\partial p_e}{\partial v} = 0, \quad . \quad . \quad (15)$$

which becomes

$$v \frac{\partial p}{\partial v} - M_a \cdot \psi_2(v_a) \frac{\partial \{p_a \cdot \psi_1(T, p_a)\}}{\partial v} - M_e v_e \frac{\partial p_e}{\partial v} = 0, \quad (16)$$

by means of equations (13) and (14). From the second cycle two additional equations may be obtained in which the independent variables are M_a and M_e .

The subsidiary equations that are used to solve these equations are independent of the molecules c in the chamber C_a . It follows, therefore, that the expression obtained for the constant of mass action will contain the functions ψ_1 and ψ_2 . An examination of the investigation in the paper quoted will

* Phil. Mag. vi. pp. 195-203 (1928).

† Phil. Mag. v. pp. 620-629 (1928).

show that in that case the constant of mass action is a function of the volume and masses of the constituents as well as of the temperature. Thus, for example, equation (15) in that paper, which corresponds to the reaction



now becomes

$$\int \left\{ \psi_2 \left(\frac{1}{C_a} \right) \frac{\partial \{ RTC_a \cdot \psi_1(T, RTC_a) \}}{\partial C_a} + \frac{1}{C_a} \right\} \partial C_a \\ = \log \frac{1}{v} + \psi_3(M_a, T). \quad . \quad . \quad (18)$$

If this is integrated and the expression obtained for C_a substituted in the equation

$$K \left(\frac{M_a}{v} - C_a \right) = C_a^2, \quad . \quad . \quad . \quad . \quad (19)$$

obtained from equations (10) and (11) in the paper quoted, the functional nature of K with respect to v is obtained.

It will be of interest to consider the special case corresponding to the concentration of the substance a in the chamber C_a obeying Henry's law, in which case we have $p_a' = \alpha_1 p_a$ and $v_a' = v_a / \alpha_1$ where α_1 is a constant. Equation (15) now reduces to the same form it would have if no molecules c were present in the chamber C_a . Hence under these conditions the molecules c have no catalytic effect on the constant of mass action.

§ 5. *The Functional Nature of the Constant of Mass Action of Electrolytes.*

Let us suppose that the apparatus in the figure is placed in a solvent to which the walls are permeable, and that the chamber C_{ae} contains a mass M of a solute which dissociates in part into positive and negative ions. Let us also suppose that the membranes separating this chamber from the chambers C_a and C_e are permeable to the positive and negative ions respectively. The pressures p_a , p_e , and p now denote the osmotic pressures of the segregated ions, and of the mixture of undissociated solute and ions, respectively.

The ions in a solution due to the dissociation of an added solute, behave as a whole like uncharged molecules as far as their intrinsic pressure is concerned, since the repulsion the ions of one sign exert upon each other can be shown to be balanced by the attraction the ions of opposite sign exert upon each other. Thus consider the solution divided into two parts A and B by an imaginary plane. Let the negative

ions in A repel the negative ions in B with a force F . The positive ions in the two parts will then repel each other also with a force F . Hence the part A repels the part B with a force $2F$. But the negative ions of A attract the positive ions of B with a force F , and the positive ions of A attract the negative ions of B with a force F , or the two parts attract each other with a force $2F$. This force of attraction neutralizes the force of repulsion. Thus the total effect of the electric charges of the ions on their intrinsic pressure is zero. As a first approximation the ions may therefore be taken to behave like uncharged molecules, and hence, if the concentration is not too large, the osmotic pressure of the mixture of solute and ions in the chamber C_{ae} approximately obeys the gas laws.

The pressures of the positive and negative ions in the chambers C_a and C_e are equal to the pressures of the corresponding ions in the chamber C_{ae} . For, if that were not so, diffusion from one chamber to the other would take place. We may therefore write

$$p_a = p_e = CRT \quad . \quad . \quad . \quad . \quad (20)$$

for these pressures, where C denotes the concentration of the positive and negative ions in the chamber C_{ae} .

Some information about the concentration of the ions in the chambers C_a and C_e may be obtained from the following considerations:—Let us suppose that each molecule of solute in the chamber C_{ae} is dissociated into two ions, each of which carries a charge e , and let them be transferred at constant pressures into the chambers C_a and C_e . The external work done on the system is

$$pv - 2p_a v_a M,$$

where v_a denotes the volume of a mol of ions in both the chambers C_a and C_e , and M the mass in mols of the original solute. But since the solute is completely dissociated, and the pressure of each kind of ion is the same in the chambers C_a , C_e , and C_{ae} , the foregoing work may be written

$$2p_a(v - Mv_a).$$

If the volume of each of the chambers C_a and C_e at the end of the process is the same as that of the volume of the chamber C_{ae} at the beginning, $v - Mv_a = 0$, and hence the foregoing work is zero. But it cannot be zero, and has besides a positive value, since this operation involves the separation of positive from negative ions. It follows, therefore, that

$$Mv_a < v,$$

or the concentrations of the ions in the chambers C_a and C_e are greater than the corresponding concentrations in the chamber C_{ae} . Since the work of separation of the ions in the chamber C_a from those in the chamber C_e against electrical attraction increases with their concentrations and these concentrations increase with the corresponding concentrations in the chamber C_{ae} , the above work done increases with increase of the latter concentrations. Hence the ratio Mr_a/v decreases with decrease of v . We may therefore write

$$v_a = v_e = \frac{\alpha_2}{C}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where α_2 is a function of C which is smaller than unity, and which decreases with an increase of C .

The reason for this difference in concentrations is probably that when the ions are of one sign and two ions approach one another they decrease in speed on account of the repulsion they exert upon each other, and the average velocity of translation is thus smaller than would otherwise be the case. The concentration corresponding to a given pressure will then be greater than when the particles are uncharged. The effect is the opposite to that existing with uncharged molecules, in which case the attraction they exert upon each other increases their average velocity of translation*. This would be for large concentrations considerably greater than that corresponding to the gaseous state. The latter velocity a molecule has when it passes through a point in the substance at which the forces of the surrounding molecules neutralize each other. In the case of a mixture of equal numbers of positive and negative ions the decrease in velocity when two similarly charged ions approach each other is compensated by the increase when two ions oppositely charged approach each other.

The osmotic pressure p of the mixture in the chamber C_{ae} is given by

$$p = RT(C'_s + 2C) = RT\left(\frac{M}{v} + C\right), \quad . \quad . \quad (22)$$

where $\frac{M}{v} - C = C_s$, the concentration of the undissociated solute. On substituting for p, p_a, p_e, v_a , and v_e in equation (1)

* 'A Kinetic Theory of Gases and Liquids,' by R. D. Kleeman, Chap. II. (John Wiley & Sons, New York). Phil. Mag., July 1912, p. 100.

from equations (22), (21), and (20), and taking into account the equations $M_a = M_e = M$, we obtain

$$\frac{\partial C}{\partial v} = \frac{MC}{(Cv - 2M\alpha_2)v} \cdot \cdot \cdot \cdot \quad (23)$$

This equation, together with the mass action equation

$$KC_s = K\left(\frac{M}{v} - C\right) = C^2, \cdot \cdot \cdot \cdot \quad (24)$$

determines the functional form of K . An equation may be obtained from this equation by differentiation with respect to v , which may be written

$$\begin{aligned} \frac{\partial K}{\partial v} &= \left[\frac{\partial}{\partial v} \left(\frac{C^2 v}{M - Cv} \right) \right]_c + \left[\frac{\partial}{\partial C} \left(\frac{C^2 v}{M - Cv} \right) \right]_v \frac{\partial C}{\partial v} \\ &= A_1 + B_1 \frac{\partial C}{\partial v}, \cdot \quad (25) \end{aligned}$$

and by the help of which the properties of K may conveniently be investigated.

Let us first consider the case corresponding to the dissociation of the solute in the chamber C_{ae} being small, in which case C is small. The quantity α_2 in equation (23) is then equal to unity. If the expression for $\frac{\partial C}{\partial v}$ given in that case

by equation (23) is substituted in equation (25), we obtain $\frac{\partial K}{\partial v} = 0$, as has already been shown in a previous paper*.

Thus in the case of weak electrolytes K is a constant at constant temperature, which agrees with the facts.

If, however, the ionic concentration is large, as with strong electrolytes, α_2 is less than unity. Now, the values of A_1 and B_1 in equation (25) are positive, and the value of $\frac{\partial C}{\partial v}$ given by equation (23) is negative when $\alpha_2 = 1$. These values, we have just seen, reduce the right hand side of equation (25) to zero. When α_2 is less than unity the negative value of $\frac{\partial C}{\partial v}$ given by equation (23) is greater than that corresponding to $\alpha_2 = 1$. In that case the value of $\frac{\partial K}{\partial v}$ given by equation (25) is negative. This agrees with the

* Phil. Mag. v. pp. 620-629 (1928).

facts according to which $\frac{\partial K}{\partial v}$ in the case of strong electrolytes

has decided negative values. This is indicated by the values of K given in the Table (see p. 659), where the first column gives the volume in litres of the solution containing a mol of KCl , the second column the value of Cv , and the third column the values of K calculated by equation (24) *.

A further test of the theory may be made by calculating the value of α_2 given by equation (23) corresponding to different ionic concentrations in the chamber C_{ae} . Its values should be less than unity and decrease with increase of concentration. Thus it was obtained from the Table that, corresponding to the volumes 7500 and 1.5, α_2 has the values .98 and .88 respectively. Corresponding to the volume 7500 the value of α_2 is nearly equal to unity, as we would expect should be the case at such low concentrations. A striking confirmation of the theory is thus obtained.

If the functional form of α_2 were known equation (23) could be integrated, and hence the functional form of K be determined from equation (24). But the exact form of α_2 cannot at present be predicted theoretically. We may therefore proceed to determine the functional form of K empirically from the values of K and v given in columns 1 and 3 of the Table. If we write

$$K = \frac{2.35}{v^{.5459}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

and calculate the values of K corresponding to the various values of v in the first column of the Table, the values given in the fourth column are obtained. A more complicated formula for K would no doubt give a better agreement with the facts †. The exponent of v in the foregoing equation is approximately equal to $\frac{1}{2}$, which is probably not accidental but has an important significance.

* Table taken from 'A Treatise on Physical Chemistry,' p. 557, edited by H. S. Taylor (D. van Nostrand Co., New York), which was compiled from figures by Kohlrausch and Maltby, *Wiss. Abh. tech. Reichsanstalt*, iii. p. 157 (1900).

† Strictly equation (26) should be written $K = a + \frac{b}{v^c}$, where a is the limiting value of the constant of mass action when the concentration is infinitely small, and which accordingly is a function of the temperature only. But since the value of a is small in comparison with a large range of values of the other term, its value probably cannot be determined very accurately from this equation.

TABLE.

<i>v</i> lit.	Cv.	K.	$\frac{2.35}{v^{.5459}}$
∞	1.000	—	—
10,000	.9936	.0154	.0154
5,000	.9912	.0223	.0225
2,000	.9862	.0352	.0371
1,000	.9802	.0485	.0542
500	.9723	.0681	.0790
200	.9577	.1084	.1303
100	.9424	.1542	.1892
50	.9234	.2221	.2892
20	.8910	.3642	.4582
10	.8624	.5405	.6686
5	.8310	.8154	.9761
2	.7883	1.434	1.610
1	.7565	2.350	2.350

It appears, therefore, that *when an electrolyte dissociates easily into ions the constant of mass action is a function of the volume of the solution as well as of the temperature.* This signifies that *either the chance of a molecule dissociating into ions depends on its previous encounters with other molecules, or that the chance of two ions of opposite sign combining on collision depends on previous encounters with other ions and molecules, or that both effects occur.*

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LXI. *Covalency, the Paramagnetism of Oxygen and Stereochemistry.* By H. F. BIGGS, M.Sc., M.A., Demonstrator in Physics in Oxford University*.

LONDON'S† theory of covalency suggests so many more researches both theoretical and experimental than I shall be able to carry out, that I venture to publish the following somewhat speculative considerations.

London shows by very general arguments as to symmetry that two atoms will form a homœopolar or covalent link

* Communicated by Prof. Townsend, F.R.S.

† *Zts. f. Phys.* xlv. p. 455 (1928).

when each possesses an unpaired electron, if these electrons are in corresponding orbits but spinning opposite ways. The "correspondence" of the orbits includes angular momentum and orientation, but perhaps not radial motion. Further, in any atom in a group of orbits with the same azimuthal quantum number the unpaired electrons all spin the same way.

London writes for the six outer or L electrons of the oxygen atom :

	<i>s</i>	<i>p</i>		
<i>l</i>	0	1		
No. of electrons	2	2	1	1

where *l* is the old azimuthal number (*k*) minus one. The two unpaired electrons in differently oriented orbits are the valency electrons. Now, if the axes of the four *p*-orbits are arranged thus :



the resultant is one unit of angular momentum, giving a P term, while the two spins, combining in the same direction to give again one unit, may make an angle of 0° , 120° , or 180° with the doubled orbit, giving a final resultant $j=2, 1$, or 0 respectively, thus forming a triplet P term as seems to be required by observation. There is nothing new in this ; it is only a consistently geometrical statement of the known model. If we now form an oxygen molecule we place two such atoms in the same orientation, which will be symmetrical to the line of their nuclei. The odd spins then go out in pairs (forming the bonds), but we are left with a resultant *orbital* angular momentum of 2 units. Since this is due to electrons describing *p*-orbits, we may suppose that in a magnetic field the whole molecule will be oriented parallel, perpendicular, or anti-parallel to the field, giving a Stern-Gerlach triplet, with splitting-factor 2, if we assign

one Bohr magneton to each p -orbit. This gives the right value for the paramagnetism of oxygen on Sommerfeld's* quantization of Langevin's Theory, namely :

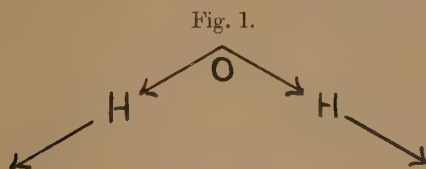
$$\chi = \frac{2^2 + 0^2 + (-2)^2}{2} \frac{N\beta^2}{kT},$$

$$\kappa = 1.42 \times 10^{-7} \text{ at } 20^\circ \text{C. ; } (\kappa_{\text{obs.}} = 1.44 \times 10^{-7}),$$

where χ is the molecular susceptibility and κ the volume susceptibility, N is Lohschmidt's number and β is one Bohr magneton, while the numerical fraction represents the mean square of the component of magnetic moment parallel to the field.

Van Vleck's† detailed theory also needs only a slight modification to fit this model, for we obtain the same result if in his formula (27) or (28) we put the spin-number s equal to zero, and instead of σ_k^2 write $\sigma_k(\sigma_k + 1)$, as is justified by his own reasoning (p. 606, *l. c.*).

The 120° between the orbits of the p -electrons in the oxygen atom has now obvious applications in chemistry, for the water molecule must be drawn thus :



which gives a dipole moment and may underlie the hexagonal structure of ice. We here make the natural assumption that when two atoms are joined by a single bond, the line of nuclei is the common axis of the valency orbits. A closed chain of three atoms suggests itself for ozone, but we have then to assume that *parallel orbits may give rise to a bond, even when the spins are not directly opposed*, since otherwise no closed chain of an odd number of atoms could be formed by London's covalent links.

For the nitrogen atom we should have two paired s -electrons, and the three p -orbital axes making 120° with each other in a plane. The nitrogen molecule would then obviously be neutral (or diamagnetic), while the NO molecule would have one orbital magneton and one spin

* 'Atombau,' 4th edition, pp. 639 and 641.

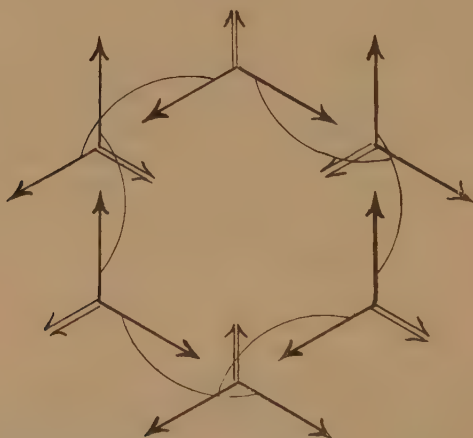
† Phys. Rev. xxxi. p. 587 (1928).

magneton, presumably parallel or anti-parallel, which, when quantized as for O_2 would give for the susceptibility

$$\chi = \frac{2^2 + 0^2 + 0^2 + 0^2 + 2^2 + 0^2}{6} \cdot \frac{N\beta^2}{kT}, \kappa = \cdot 71 \times 10^{-7} \text{ at } 20^\circ \text{ C.},$$

or half the value for oxygen. This number is also obtained by Van Vleck, but it does not agree with the available observations ($\kappa_{\text{obs.}} = \cdot 61 \times 10^{-7}$), and Van Vleck accounts for the discrepancy by introducing another factor depending on the temperature, which for nitrogen will have the required value of 0.85 at ordinary temperatures, while for oxygen it is practically unity, the distinction between the

Fig. 2.



two cases being due to the energy intervals being comparable to kT in the case of nitrogen but not in that of oxygen. In the case of the present model, however, this distinction can hardly be supposed to hold, and therefore the agreement of the model with observation must be regarded as unsatisfactory.

Carbon, again, is given by London one s -electron and three unpaired p -electrons, which I arrange at 120° with each other in a plane. If, then, one of the p -bonds is used up on a hydrogen atom, the axes of the remaining two valency orbits of each CH radical will form an angle of 120° . Six such radicals can now combine without strain to form a plane regular hexagon as in fig. 2, where the whole arrows

represent orbital axes, the half arrows spin axes, and the curved lines bonds between electrons whose orbits are parallel but whose spins make 120° with each other. The spins may also be alternately in opposite directions as we go round the ring. All this time we are conveniently neglecting the six *s*-electrons, but I suggest that since there is nothing directional about the *s*-state (it is really not an orbit at all), the direction of spin is free, and the bond can have perhaps an attractive but no directive effect, and may be neglected in building simple molecules. The only strong reason I can think of against such an assumption is that the hydrogen molecule is apparently held together by *s*-electrons. In most other cases when an atom has a single outer electron in an undoubted *s*-state, as in the case of the alkalis, this electron does not form a covalency, but drops off. In graphite the *s*-electron would form the bond normal to the planes of cleavage, accounting for the lubricating properties of the substance.

Diamond and the aliphatics, on the other hand, seem quite inexplicable on this model, and all four *L*-electrons must have $l = 1$ and have their orbit-axes pointing in tetrahedral symmetry. If this is correct, the inert gases might also be taken to have their outer electrons arranged in pairs with the axes of their orbits in tetrahedral symmetry.

Such a model is, of course, contrary to the accepted spatial quantization, which only allows three different *p*-orbits; but it does not seem necessary that in the quantization of a system of several electrons the only possible states of the individual electrons should be those of an electron in a system or "ring" by itself. The geometrical method of atom-building, however, though it justifies this model, does not account for the fact that we never get an *s*-electron when we have four *p*-electrons in tetrahedral symmetry.

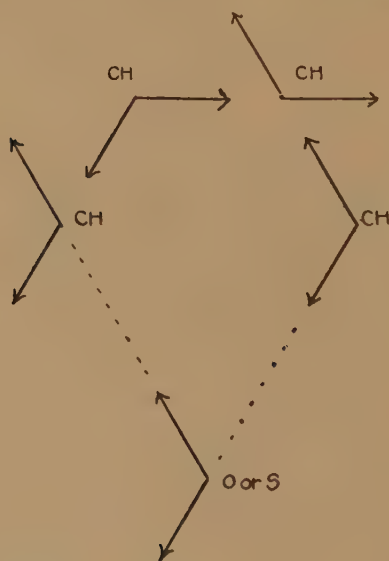
The apparent anomaly, that if benzene is forced to take up two *additional* atoms of hydrogen the C_6H_8 behaves as a far more unsaturated substance than C_6H_6 , may now be readily explained; for the additional atoms cannot be added without upsetting the hexagonal symmetry of the carbon atoms concerned, so that the unstrained plane structure of the ring is lost, and it is natural to suppose that the other carbon atoms revert to the tetrahedral type and become actively tetravalent. That the "aromatic" properties of benzene, hexagonal angles, and apparent trivalency of carbon are associated is shown by a consideration of furan or thiophen, which I draw as in fig. 3. These have properties very similar to those of benzene, and,

again, their *addition* products have no aromatic properties, but are analogous to cyclohexane.

London's hypothesis is also supported by some of the facts of catalysis. The magnetic metals are the strongest catalysts, and seem to produce their effect with only small energy change, presumably by their power of orienting the reacting molecules so that they have a greater concentration in a position favourable to reaction with each other at the surface of the metal than in the body of the gas.

A partial interpretation can now be given of the effect* of hydrogen in diminishing the paramagnetism of palladium

Fig. 3.



The magnitude of the effect is of a far higher order than the diamagnetism of hydrogen: 7.8×10^{-8} per c.c. at room temperature against 2×10^{-10} . A quantitative agreement cannot be obtained till we know something more of the mechanism of the absorption of the hydrogen; but it is evident from a comparison of the value just given with the susceptibilities of O_2 and NO that the order of magnitude is consistent with the neutralizing of two magnetons of palladium per molecule of hydrogen absorbed.

* Biggs, *Phil. Mag.* xxxii. p. 131 (1916).

LXII. *Crystal Structure of Calcium***By C. D. NIVEN, M.A. †.*

IN endeavouring to grow crystals of calcium, some were obtained which definitely showed that Hull was right in ascribing a cubic structure to calcium, and a brief description of the work will be given in the following paragraphs.

As calcium reacts with glass or other siliceous substance it is necessary in heating calcium to use containing vessels of iron. At first, an endeavour was made to make crystals by Bridgeman's ‡ method. An iron tube was closed at one end by screwing on a cap, and pieces of calcium were dropped in. The air was then evacuated and the iron tube closed at the top by a rubber tube and clamp. The end at which the calcium was lying was then lowered into a furnace. It was found that after heating strongly and cooling, the calcium took on the appearance of having been melted, but yet it had not run to the bottom of the tube. Calcium was also placed in a pyrex glass tube and heated, although it attacked the walls of the tube very badly, making them quite black, yet when the tube was broken crystals of metal could be found inside on the walls of the tube. It appeared from this that calcium had a very low distillation temperature, and that it might be quite possible to get crystals by distillation.

The furnace which had been previously used by Professor McLennan and the author in distilling lead was accordingly fitted up again. Improvements were made in regard to keeping the outer case of the furnace cool. A window was put into the side so as to see the furnace as it heated, and the molybdenum strip was replaced by a new form of heating element. This consisted of a piece of nichrome wire wound round an iron crucible. The crucible consisted of a piece of half-inch iron rod about two inches long, bored out so that the walls were about $1/32$ inch thick. In order to insulate the nichrome wire from the iron, alundum powder was mixed up with water glass to form a thin paste, and smeared over the outside of the iron crucible. It was allowed to dry overnight, preferably in a warm place. About 17 turns of nichrome wire (18-wire gauge) were

* This work was carried out with the aid of a Fellowship from the National Research Council of Canada.

† Communicated by Prof. J. C. McLennan, F.R.S.

‡ Proc. Amer. Acad. of Arts & Sci. lx. p. 305 (Oct. 1925).

coiled round the crucible, the turns being closer together at the bottom than at the top, and in order to keep in the heat more of the water glass preparation was put on the outside. At first a small condenser was arranged just above the mouth of the crucible, but it was found that a little iron lid, with a hole through it for evacuation purposes, served quite sufficiently to condense the distilled calcium.

The current was read on an ammeter, and tests were made with currents from 10 to 15 amperes.

It was easy to see with the naked eye that the crystals formed were not hexagonal as H. Moissan * had concluded. The four-sided pyramids could easily be seen, yet it was hard to say definitely whether they were tetragonal or cubic. To do this it was necessary to make a goniometer measurement, which was very kindly performed by Professor A. L. Parsons, of the Mineralogical Department, University of Toronto. The values of ρ and ϕ found are given in the table, and clearly demonstrate that the crystal was a rhombic dodecahedron. The crystals of calcium were found to stand considerable exposure to the atmosphere.

ρ	45° 00'	45° 09'	45° 03'	45° 05'
ϕ	180° 02'	359° 56'	90° 01'	270° 00'

In conclusion, I should like to express my sincere thanks to Professor Parsons for his kind assistance in identifying the crystal form, and to Professor McLennan for stimulating suggestions throughout the work.

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University of Toronto.

LXIII. *Electrical Conductivity of Arsenic and Antimony at Low Temperatures* †. By Prof. J. C. McLENNAN, F.R.S., C. D. NIVEN, M.A., and J. O. WILHELM, M.A. ‡

AT the present time it is generally conceded that superconductivity is a property only of certain elements. In view of this fact the efforts of the authors of this com-

* *Comp. Rend.* cxxvi, p. 1753 (1898).

† This work was carried out with the aid of a grant of a Fellowship from the National Research Council of Canada to C. D. Niven.

‡ Communicated by the Authors.

munication have been directed recently towards finding the actual temperature-resistance curves at low temperatures of the metals investigated, rather than towards merely trying whether a particular metal was superconducting or not. Most experimenters seem to have been bent on finding superconductors, so that a great deal of work has been done on the more electropositive metals at very low temperatures, while very little has been done on such metals as arsenic and antimony. So far as theory is concerned this has not been advantageous, as the electropositive elements have fewer valency electrons and are therefore simpler; yet, before any theory can be complete, it must apply to those metals with higher valency and more complicated crystal structure. With this in mind, the authors carried out the work described below on arsenic and antimony.

Arsenic.

As crystal structure has undoubtedly a certain bearing on the electrical resistance of a piece of metal, it was thought desirable, if possible, to get a single crystal of arsenic, and a considerable amount of time was spent in this connexion. Arsenic, when heated, sublimes before it melts, and on this account it was not possible to make crystals by Bridgeman's* method, which, briefly, consists of lowering the metal contained in a glass tube slowly out of a furnace into the cool air of the room. When this was done the metal condensed much too rapidly and a deposit that was not a crystal was formed. It was quite impossible to prevent this condensation by merely lowering the tube slowly. But the experiments made in attempting to do this suggested to us two methods of making crystals of arsenic, one of which was subsequently adopted.

Before we describe the different tubes in which the metallic arsenic was contained, a short description of the furnace used will be given, as the detailed construction of it was a little different from that of the one Bridgeman used. Instead of taking a quartz tube and winding resistance wire round it, we took six porcelain heating coils as used in domestic room-heaters, and placed these on end. In order to hold them in position, pieces of channel-shaped porcelain were tied round them with wire and the whole embedded in fireclay inside two channel-shaped pieces of asbestos used for lagging steam pipes. The terminals of the six heating coils were connected in parallel to two heavy brass rods suitable for carrying the current. The whole

* Proc. Am. Acad. of Arts and Sc. lx. p. 305 (Oct. 1925).

thing was then placed inside a sheet tin case, which had a hole in the top and in the bottom. Asbestos was packed in to hold the furnace central in the case, and the top was then soldered on. The case was in turn mounted on a wooden stand, so that it could turn and thus allow the furnace to lie in a vertical or a horizontal position. In using this type of furnace it is important to note that the temperature reached with a given current is very different when the furnace is standing in a vertical position with the ends open, from what it is when in a horizontal position, owing to the fact that in the vertical position there is a strong circulation of air.

There was no particular reason for constructing the furnace out of these heating coils beyond the fact that there was no quartz of the required size on hand at the time, and there was no reason for leaving the little air space between the porcelain packing and the coils, except that it was thought that the air space would conduct away a little less heat than fireclay or porcelain. Yet these two factors contributed to making the temperature of the furnace uneven along the inside. Wherever there was a junction of two heaters, the temperature was a little lower than in the middle of a single heater. Although it was by accident that the furnace was constructed with this unevenness of temperature, it was subsequently found to be the key to getting crystals to grow.

The tubes in which the arsenic was placed were made at first as follows. A piece of pyrex glass about 8 inches long and 0.75 cm. in diameter was sealed up at one end. A smaller tube was sealed into the side and bent round till the small tube pointed along the axis of the larger. The end of the smaller tube was sealed up, and the arsenic placed in the pocket formed at the bottom of the larger tube; the whole tube was then evacuated and sealed off at the top. It was hoped that when the tube was suspended, the arsenic would slowly distil to the bottom and form a crystal there. Instead of this happening, it was found that, while some of the arsenic found its way to the lower parts of the short tube and condensed merely on the side, yet a crystal was formed in the bend of the small tube. It was noticed, too, that the mass of arsenic in the pocket gradually took on a crystal-like appearance against the glass. The "arrangement" of the mass of arsenic into a crystal was similar apparently to the phenomenon observed by Langmuir in making copper crystals. This method of holding the metal at a high temperature until a crystal is formed, appeared therefore to have possibilities in the case of arsenic, but we did not pursue the method, as it was found possible to get a large

enough crystal out of the small tube for measuring change of resistance with temperature. The actual crystal measured was taken from a tube such as the one just described. Even when the tube was suspended for a long time in the furnace it was noted that the arsenic did not all distil into the small tube at the bottom, and at first it seemed surprising that the crystal referred to above was formed near the top of the small tube at all. It was concluded that if the furnace had been made of one piece instead of a number of small pieces this could not have happened; but because of the particular way in which our furnace was accidentally constructed, cool parts existed at the junctions of the heated coils. The temperature at such a point must have been sufficiently high for the slow formation of the crystal, and not too high to cause it to distil away again from that part of the tube.

Subsequently the furnace was turned into a horizontal position and merely a straight tube containing arsenic at one end was pushed in. The arsenic sublimed from the warmer part of the tube to the cooler part which lay opposite a junction of two coils in the furnace. Various methods were employed to try and improve on the type of tube for forming the crystal, such as introducing a current of air in an inner tube inside the tube containing the arsenic; the condensation, however, was too rapid, with the result that a number of small crystals were formed instead of a single large one. The improvement that seemed necessary was to construct a furnace with two chambers which could be regulated separately and fitted with thermometers to tell just the correct temperatures for the best formation of crystals, but as our object was mainly to get a single crystal for electrical measurements and not to grow large crystals, we did not continue farther with the work.

The crystal to be measured was clamped between two copper jaws at either end. Four wires leading to the four jaws comprised the two current leads and the two potentiometer leads. Crystals formed from the vapour of a substance display their facets and thus differ as a general rule from crystals formed by slow cooling of molten metal. In one of our crystals the direction of the hexagonal axis could be easily seen. Measurements were made on this crystal between room temperature and the temperature of liquid helium along the hexagonal axis.

Antimony.

No trouble was experienced in making a crystal of antimony from molten metal. In spite of the fact that antimony has a melting-point nearly as high as pyrex glass,

it was found that a fine bore tube did not cave in at the temperature of molten antimony and that it was possible to obtain a long thin single crystal by the method used by Bridgeman in pyrex glass. The temperature resistance curves of a crystal of antimony prepared in this way and also of a chip off a mass of metal were investigated between room temperature and the temperature of liquid helium.

Results of Measurements.

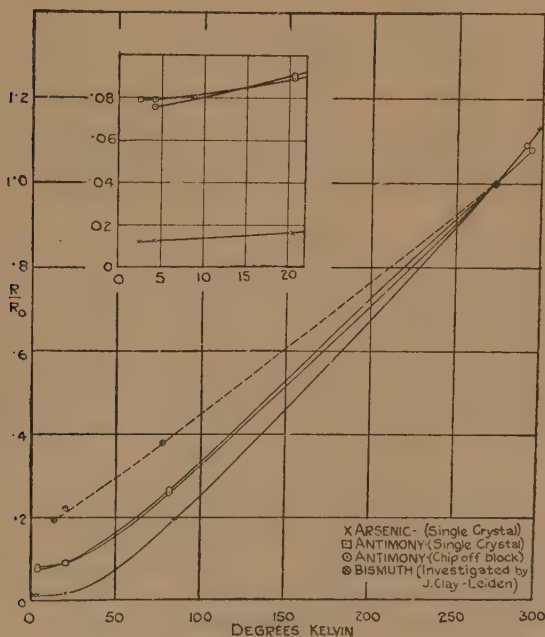
In the work previously published by the authors, graphs, showing the variation of electrical resistance with temperature, have been constructed measuring specific resistances along the resistance axis. In this communication, however, the more usual practice of using the ratio of the resistance at any temperature to the resistance at 0°C. will be adopted. We do this because we wish to compare our results with Clay's*. The results of the measurements are given in the table, and these are presented in graphical form in the diagram.

Crystal of Arsenic.					
Degrees Kelvin.		Ohms.	R/R_0 .		
298		1.25×10^{-3} .	1.13		
273		1.11	1.00		
85		.216	.195		
20.6		.018	.0162		
4.2		.014	.0127		
2.42		.014	.0127		

Chip of Antimony.			Crystal of Antimony.		
Degrees Kelvin.	Ohms.	R/R_0 .	Degrees Kelvin.	Ohms.	R/R_0 .
294	8.28×10^{-4} .	1.08	291	7.97×10^{-3}	1.09
273	7.66	1.00	273	7.32	1.00
82	2.03	.265	82	1.90	.260
20.6	.696	.0909	20.6	.656	.0896
4.2	.580	.0760	4.2	.579	.0791
			4.43	.581	.0794

* Diss. Leiden, 1908, p. 51.

By studying the diagram below we can reach some rather interesting conclusions. (1) The resistance temperature curve of the antimony crystal is not very different from that of the piece off the mass of metal. (2) The curves arrange themselves as would be expected from the arrangement of the metals in the periodic table. (3) The temperature resistance curve for arsenic resembles that of many other pure metals. At the same time there is a very decided



departure from the law stating that the electrical resistance is proportional to the absolute temperature. (4) Our results show that in the case of both arsenic and antimony resistance at low temperatures approximates to a definite residual value. This property is common to most pure metals. The arsenic crystal was measured to 2.42°K. , and the antimony crystal to 2.43°K. ; neither was found to be superconducting.

On the graph we have drawn the curve for bismuth according to Clay's results; bismuth appears to be unique in its behaviour, since, so far as is known, it is the only

pure metal that has a value of R/R_0 greater than 0.3 at the temperature of liquid air. The value 0.3 is what would be expected if the linear relation connecting resistance and temperature held good. In general, metals have a value of R/R_0 in liquid air less than 0.3, and in this respect both arsenic and antimony follow the general behaviour of other metals.

The Physical Laboratory,
University of Toronto.
June 30th. 1928.

LXIV. *The Resistance of Cæsium, Cobalt, and Chromium at Low Temperatures.* By Prof. J. C. McLENNAN, F.R.S.,
C. D. NIVEN, M.A. *, and J. O. WILHELM, M.A. †

Cæsium.

ALTHOUGH a great deal of work has been done on the conductivity of the alkali group of metals in regard to variation with both temperature and pressure, yet data were not available on cæsium and rubidium below the temperature of liquid air at the time when Onnes and Tuyn‡ published their "Data concerning the Electrical Resistance of Elementary Substances at Temperatures below $-80^{\circ}\text{C}.$ " Last year the authors of this communication published some data on rubidium at low temperatures, so that only cæsium remained to be measured.

The cæsium was run into a fine capillary tube similar to that used in measuring potassium and sodium, as described in another paper§. Measurements were made at room temperature and at the temperature of liquid air, liquid hydrogen, and liquid helium. By assuming the value for the specific resistance given in Smithsonian Tables and by neglecting any change in the dimensions of the cæsium due to contraction with change of temperature, the values of the specific resistances were calculated. The results are given in Table I. and reproduced graphically in the diagram (p. 674).

* This work was carried out with the aid of a Fellowship from the National Research Council of Canada to C. D. Niven.

† Communicated by the Authors.

‡ Leiden Communications Supplement, No. 58.

§ Phil. Mag. iv. p. 386 (Aug. 1927).

TABLE I.

Cæsium.			Chromium (aged).		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
290	75.34×10^{-3}	205	292	5.59×10^{-3}	17.2
82	18.50	5.04	80	.655	2.01
20.6	4.69	1.28	20.6	.260	.80
4.2	1.32	.359	4.2	.258	.79
2.2	1.19	.324	2.25	.258	.79

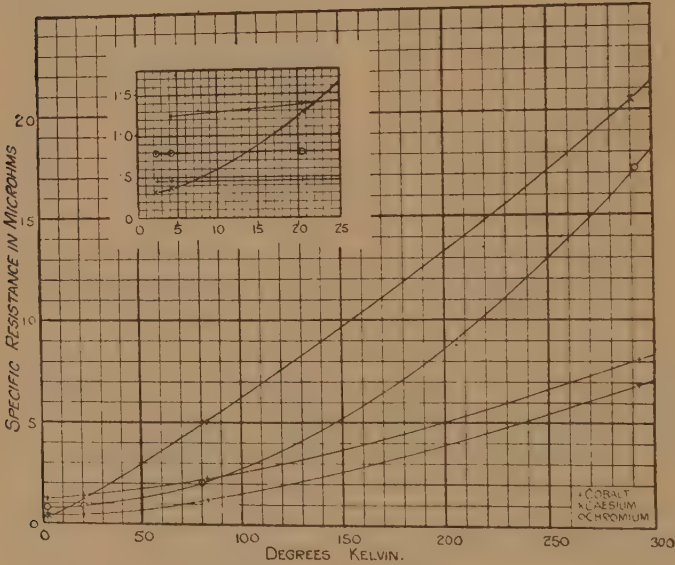
Cobalt (unaged).			Cobalt (aged).		
Degrees Kelvin.	Ohms.	Specific Resistance.	Degrees Kelvin.	Ohms.	Specific Resistance.
293	1.80×10^{-3}	8.07	293	2.11×10^{-3}	6.85
83	.495	2.22	83	.382	1.24
20.6	.313	1.37	20.6	.143	.46
4.2	.277	1.24	4.2	.140	.45
			2.5	.140	.45

P. W. Bridgeman* found that cæsium was very compressible, and also that the electrical resistance passed through a minimum with increasing pressure, and on this account cæsium appeared to be an interesting member of the alkali group to measure at low temperatures. The resistance of nearly all pure metals, other than superconductors, approaches a certain limiting value, so that in general at very low temperatures the resistance of a pure metal is independent of the temperature. In this respect cæsium stands out as different from most pure metals. A glance at the diagram shows that the resistance of cæsium continues to decrease with temperature below 4° K.

In Table II. values of R/R_0 —i.e., the ratio of the resistance at any temperature to the resistance at 0° C.—are

* Am. Acad. Proc. lx. pp. 385-421 (Oct. 1925).

given for sodium, potassium, rubidium, and caesium at the temperatures of liquid hydrogen and helium. It can be observed from these figures that the three metals, sodium, potassium, and rubidium, all approach a certain limiting value. Had caesium behaved like rubidium a limiting value



of about $\cdot 046$ might perhaps have been expected. Spectroscopic data give the following electronic configurations* for the alkalis.

TABLE II.

	Sodium.	Potassium.	Rubidium.	Cæsium.
0° C.	1	1	1	1
Liquid hydrogen ...	$\cdot 015$	$\cdot 027$	$\cdot 057$	$\cdot 067$
Liquid helium	$\cdot 004$	$\cdot 007$	$\cdot 038$	$\cdot 018$
Liq. hel. red. pr. ...	$\cdot 004$	$\cdot 007$	$\cdot 038$	$\cdot 017$

* See paper by McLennan, Smith, and McLay, Proc. Roy. Soc. A, cxii. p. 76 (1926).

Sodium 2 : 2.6 : 1.

Potassium... 2 : 2.6 : 2.6 - : 1.

Rubidium ... 2 : 2.6 : 2.6.10 : 2.6 - - : 1.

Cæsium..... 2 : 2.6 : 2.6.10 : 2.6.10 - : 2.6 --- : 1.

When the valence electron is stripped off the core is left complete in the case of sodium, potassium, and rubidium, but in the case of cæsium the fourteen 4_4 electrons are missing. It is highly probable that this accounts for the compressibility of cæsium, and it is not improbable that it accounts too for the temperature gradient of the electrical resistance persisting right down to very low temperatures. This explanation would be more feasible if rubidium had had a limiting resistance comparable with that of sodium or potassium, but measurements do not indicate that this is the case. Cæsium was not superconducting at the temperature of 2.2° K.

Cobalt and Chromium.

A group of elements that seem so far to have been rather neglected in work on electrical conductivity are those grouped round iron. Doubtless this was due to the difficulty in obtaining pure samples, but last year, through the kindness of Mr. C. C. Paterson, a piece of pure chromium was obtained from the General Electric Company of England, and this year some pure cobalt was obtained from the Belgo-American Trading Corporation, New York. The cobalt was cut into a strip and aged in a vacuum for about four hours at a dull red heat. Measurements were made on an aged and on an unaged sample. The results of the measurements are given in Table I. and reproduced in graphical form in the diagram. It may easily be seen that the ageing had the effect of merely shifting the temperature resistance curve down in the direction of the resistance axis. The value found for the specific resistance of the aged cobalt at 20° C. was 6.85 microhms per c.e., and the specific resistances at different temperatures were calculated from this value. The specific resistance of the unaged piece of cobalt was found to be 8.07 micrhms per c.e. at 20° C.

The work on chromium has been described in a previous paper, but at the time when that paper was written it was not possible to get the final measurement in liquid helium and so the results are repeated here with that reading added. The chromium was measured at 2.25° K. and the cobalt at

2.5° K. ; neither was found to be superconducting. It was found that both cobalt and chromium had very small temperature gradients below the temperature of liquid hydrogen. It appeared, in fact, that the resistance of cobalt or chromium at low temperature was almost independent of temperature.

TABLE III.

	Chromium.	Iron.	Cobalt.	Nickel.	Copper
R/R ₀ at liq. air	·132	·0848	·202	·180	·144
R/R ₀ at liq. hydr.	·059	·0113	·075	·085	·0015
Sp. resist. at 273° K....	15.25	8.85	6.15	6.93	1.59
Sp. resist. at 20.6° K....	·90	·101	·46	·59	·0024

The value 6.85 microhms for the specific resistance of cobalt at 20° C. is much lower than the value given in Smithsonian tables, but is close to the accepted specific resistance for nickel at 20° C., namely 7.5. The value given for iron is 8.8. In Table III. values of R/R₀ are given for chromium, iron, cobalt, nickel, and copper at the temperature of liquid hydrogen. From these values and the specific resistances of the metals at 0° C., the specific resistances at liquid hydrogen temperature were calculated. The values are given in the lowest line of the table. The values for R/R₀ at liquid helium temperature for iron, nickel, and copper were not given in Onnes and Tuyn's data, and the original papers had not become accessible at the time of writing, so that it has not been possible to calculate the specific resistances at liquid helium temperature.

In comparing the specific resistances of different elements it is customary to compare the values either at room temperature or at 0° C. When the values differ widely it is not of much importance what temperature is taken for the comparison, but if the specific resistances are close together the order of magnitude may change at different temperatures. It is therefore of importance to decide what temperature should be chosen for comparing specific resistances ; it seems almost obvious that the ideal temperature for making a comparison would be the absolute zero. Measurements cannot be made at that temperature, but on account of the

fact that the temperature gradient is practically zero for many metals at low temperatures, one can employ measurements at slightly higher temperatures to make comparisons.

It was with this in view that the last line in Table III. was calculated. It appears that although iron is a poorer conductor than either cobalt or nickel at room temperature, yet at low temperature it is much superior. No measurements have been made on manganese, and therefore it is perhaps rather too early to press conclusions. Nevertheless, the figures seem to indicate that as one passes from chromium to copper, the resistance falls from a high value for chromium to a low one for iron, and then rises again for cobalt and nickel and falls eventually to a very low value for copper. This increase in the value of the specific resistance for iron is very interesting from the point of view of atomic structure. If the electron configuration for iron be taken as $2:2.6:2.6.6:2$, when the valence electrons are stripped off, a system of six 3_3 electrons is left. This is a comparatively stable system, although of course ten 3_3 electrons are required for complete stability. On the other hand, when two valence electrons are stripped off cobalt and nickel, a system of seven and eight 3_3 electrons is left. In the case of copper, when one valence electron is stripped off, all the ten 3_3 electrons are present, and an excellent conductor results. It appears then, for a metal to be a good conductor, the electron systems of the core must be completed. If this be so, the reason for the resistance of iron being small at low temperatures can be accounted for if six 3_3 electrons form a fairly stable system. Lund, in dealing with the magnetic properties of the rare earths, found that when six electrons had filled into the 4_4 system, the magnetic susceptibility fell almost as if fourteen electrons had completed the system. In offering this explanation for the behaviour of the electrical conductivity of the iron, cobalt, and nickel group, the possibility of any of them having three valence electrons has not been considered. It must be admitted that an assumption has been made here, but it seems a very reasonable one. The point that is stressed throughout this communication, both in connexion with the alkalis and with the iron group, is the importance of the structure of the core of the atom on the electrical conductivity of a pure metal.

LXV. *The Effect of Cadmium as an Impurity in Lead on the Conductivity of Lead.* By Prof. J. C. McLENNAN, F.R.S., C. D. NIVEN, M.A.*, and J. O. WILHELM, M.A.†

A GREAT deal of effort has been expended on obtaining pure metals for the investigation of electrical resistance at low temperatures because the important effect of impurities on electrical resistance has always been borne in mind by any experimenters in investigating whether a metal were a superconductor or not. Indeed, when a metal did not turn out to be a superconductor it was always doubtful whether or not the little impurity—which is nearly always present even in the purest attainable samples of a metal—was sufficient to account for the small resistance at very low temperatures. Recently, opinion has strongly favoured the idea that a residual resistance may be expected for most metals at the lowest temperatures. At the same time, if resistance at higher temperatures is so greatly affected by an impurity, two questions seemed to us to be worthy of investigation, firstly, whether or not a slight impurity in a superconductor spoilt its superconductivity at the superconducting temperature, and secondly, whether the temperature at which the superconductivity appeared changed with the amount of impurity.

In entering this field the authors of this communication realized the enormous complications that could arise in the results. When the metals are mixed to form an alloy they may either form a mechanical mixture or they may form a solid solution, or they may form a chemical combination. If a mere mechanical mixture were formed the mean conductivity might be expected, and when one of the constituents became superconducting probably the whole alloy would. On the other hand, if a solid solution were formed a totally different curve might be expected from the temperature-resistance curve for the pure metal, and it might be that the superconducting property disappeared altogether. Again, there was always the possibility that a solid solution at room temperature might undergo a change at low temperatures, and this introduced a further complication.

Very little work has been done on alloying superconductors. Some work has been done at Leiden‡ by

* This work was carried out with the aid of a grant of a fellowship from the National Research Council of Canada.

† Communicated by the Authors.

‡ Leiden Comm. No. 181.

Tuyn and Kamerlingh Onnes on an alloy of tin and lead, but the authors have not come across any other work. An alloy of tin and lead is an alloy composed of two superconductors, and it is not surprising at first sight that the alloy should have been found superconducting. Yet on further consideration this does not seem a necessary consequence of the mere fact that the original metals were superconductors. Had the metals formed a solid solution or chemical compound, why should we expect the alloy to be superconducting?

The problem of superconductivity has not been treated satisfactorily by any theory up to the present, and on this account there seemed to be no reason for not collecting data and ascertaining some empirical facts about the effect of adding impurities to a superconductor on its resistance at low temperatures, even though they could not be clearly interpreted.

Apart from the complications attendant on the formation of solid solutions and compounds, we realized that before any conclusions could definitely be drawn from our method of attack a great deal of work might be necessary. There are five superconductors, and with each of these probably 6 or 8 different metals should be alloyed. For each of these combinations a whole series of alloys should be prepared and have their resistance-temperature curves determined. The results, therefore, communicated in this paper must be looked upon as a mere beginning of what may be expected from a somewhat extensive programme, yet we think them of sufficient interest to publish, as they show that a metallic impurity in a superconductor will not necessarily eliminate the property of superconductivity.

The alloying metal chosen by us was cadmium and the superconducting metal was lead. We chose lead as it was possible for us to get a very pure sample of that metal from the Bureau of Standards. In some ways lead was awkward to measure at low temperatures as it became superconducting about 7°K . On this account great care had to be taken in handling the helium liquefier. It was necessary for conditions to be upset sufficiently at the nozzle so that liquid helium would not "make," and so that the temperature remained constant. A helium gas thermometer at the side of the liquefier indicated when the temperature was steady. The temperatures were read on a constant thermometer. In reading the temperatures we assumed that the temperature-resistance curve for constantan was linear between the temperatures of liquid helium and liquid

hydrogen. This assumption is justified from work by Onnes and Holst*. Due to the difficulties of holding the temperature constant and in reading its absolute value accurately, the value found for the superconducting temperature of pure lead was a little lower than what we found it two years ago, and on this account we measured the resistance of a piece of pure lead along with that of the pieces of alloyed metal. We were thus able to tell if the alloy were superconducting at the same temperature as the pure metal or not. This question was of much greater interest to us than the question of fixing the absolute value of the temperatures by which superconductivity appeared.

The cadmium was distilled as a precaution in case it was not pure, and alloys containing about 0.1, 1, and 3 per cent. of cadmium were prepared as follows:—The lead and cadmium were accurately weighed out and placed in a pyrex glass tube which was evacuated and sealed off. The tube was heated until the metals melted, and was then well shaken. In order to measure the specific resistance a part of the alloy thus formed was run into a glass tube of about 2 mm. bore through a fine constriction to keep back any surface contamination. If the dimensions of the sample were to be accurately determined, it was important to get the alloy to solidify in the tube free from pit-marks, and the tube was, therefore, placed in a furnace we had formerly used for making crystals and not merely heated in a bunsen flame. It was very important to get the glass broken off without damaging the surface. The cross section of each sample thus obtained was measured in five different places in a length of about 4 cm. The length was taken between two steel points which carried the “potentiometer” leads. In this way the specific resistances of the alloys we prepared were measured at room temperature, and we were thereby enabled to represent the temperature-resistance curves of different alloys on the same diagram.

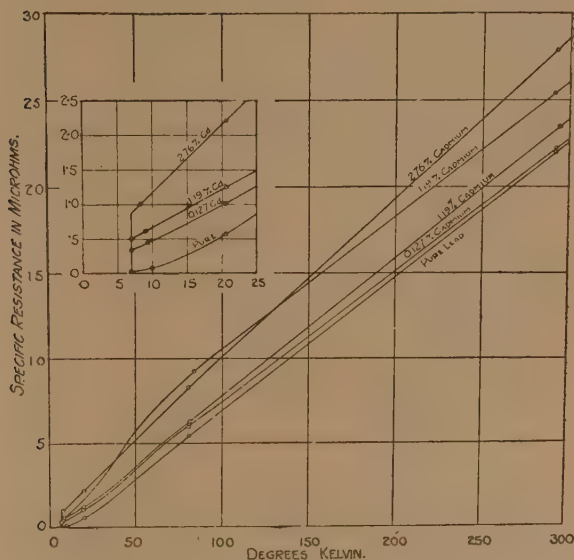
The remaining portion of each alloy was run into a fine glass tube and used for obtaining data for the resistance-temperature curves. The dimensions in this case were of no consequence; it was of greater importance to get a reasonably high value for the resistance. Pieces of two different alloys and a piece of pure lead were mounted on a piece of red fibre, and wires were soldered on in such a way that the samples were connected in series. A pair of tapping-off or “potentiometer” leads were soldered to each

* Leiden Comm. No. 141 a.

piece of metal. With this arrangement of wiring three metals could be measured with eight leads. This was a rather important point because we had only a small tube through which to bring all our wires out from the helium liquefier; in addition we had to bring out wires from the constantan thermometer.

Measurements were made at room temperature and at the temperature of liquid air and liquid hydrogen. As described above, measurements were made in the helium liquefier with the conditions upset, and it was found to our surprise that all the alloys which we had prepared were superconducting

DIAGRAM I.



at a temperature very near to that at which the pure lead was superconducting. The results of the measurements of the three alloys containing 0.127 per cent., 1.19 per cent., and 2.76 per cent. of cadmium are given in graphical form in Diagram I. A glance at the diagram shows that the curves for the alloys containing 0.127 and 1.19 per cent. of cadmium at higher temperatures run approximately parallel to the curve for pure lead, and in this respect are markedly different from the alloy containing 2.76 per cent. This appeared to us to be rather interesting, and we decided to make up an alloy containing about 2 per cent. cadmium.

As apparently all the alloys we had made so far were superconducting, we thought it would also be interesting to make up an alloy with a larger impurity still, such as 5 per cent.

Two alloys were therefore prepared, one containing 5.19 per cent. of cadmium and the other 1.88, and wires of them were mounted on the piece of fibre in place of two other alloys. They were measured at room temperature, and at the temperature of liquid air, and liquid hydrogen, and finally in the helium liquefier. With the experience we had had previously we succeeded in improving our

Specific resistances of Lead-Cadmium Alloy

Pure Lead.		0.127 % Cadmium.		1.19 % Cadmium.				2.76 % Cadmium.	
Degrees Kelvin.	Sp. resist.	Degrees Kelvin.	Sp. resist. before.	Degrees Kelvin.	Sp. resist. before.	Degrees Kelvin.	Sp. resist. after.	Degrees Kelvin.	Sp. resist. before.
293	22	293	22.2	292	25.4	294	23.5	293	27.9
81	5.46	81	5.97	84	9.27	81	6.29	81	8.34
20.6	.582	20.6	1.09	9	.620	20.6	1.24	20.6	2.22
10	.079	7.2	.359	7.2	.511			8.4	1.01
7.2	.028		Superconducting.		Superconducting.			7.2	.356
	Superconducting.								Superconducting.

technique considerably. In the first place we had learned how to control the liquefier so that the temperature remained steady for a fair length of time, and in the second place we took the leads from the pure lead to the pair of terminals on the potentiometer that we had previously been using for the standard resistance. The batteries were sufficiently constant so that when once the current was known by a measurement of the standard resistance, there was no further need of having the latter attached to the potentiometer. By having the pure lead leads attached to these terminals it was possible to switch instantaneously from the

pure lead to an alloy ; and thus, at the superconducting temperature, comparisons could be made between the pure lead and an alloy with the assurance that the temperature had not changed in the meanwhile.

With these improvements we were able to show that while the resistance of an alloy dropped suddenly at the temperature at which lead was superconducting it did not completely vanish. The 5.19 per cent. alloy became superconducting at four-tenths of a degree below the superconducting temperature of lead, and the 1.88 per cent.

before and after cooling to 7° K.

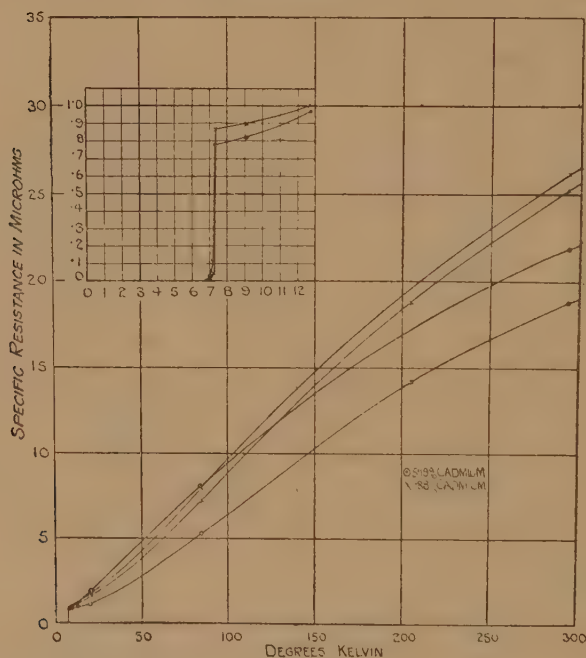
1.88 % Cadmium.				5.19 % Cadmium.			
Degrees Kelvin.	Sp. resist. before.	Degrees Kelvin.	Sp. resist. after.	Degrees Kelvin.	Sp. resist. before.	Degrees Kelvin.	Sp. resist. after.
294	26.2	294	25.3	294	21.9	294	18.8
84	8.02	225	18.8	84	8.09	225	14.2
20.6	1.75	85	7.19	20.6	1.92	85	5.29
12.7	1.06	20.6	1.54	12.7	0.97	20.6	1.08
9.1	0.90			9.1	0.82		
7.3	0.87			7.3	0.78		
7.2	0.048			7.2	0.12		
7.0	Superconducting.			7.0	0.024		
				6.8	Superconducting.		

alloy at two-tenths below. This seemed to point to the fact that the amount of cadmium affected the temperature at which the resistance of an alloy entirely vanished, but did not affect the temperature at which the phenomenon of superconductivity started to make its appearance.

From the measurements the specific conductivities were calculated and the graph was plotted. It was found that the 5.19 per cent. alloy had a very decided curvature at higher temperatures, *i.e.*, between liquid air and room temperature, and as a rough guide in drawing the curve it was decided to take a measurement in alcohol cooled

with liquid air down to about 220°K . When this was done, and the corresponding point put on the graph, it was found that we had to draw a curve with three bends in it to pass through the points. It was concluded that some mistake had been made, and as a precaution the readings in liquid air of the 1.88 per cent. and the 5.19 per cent. alloys were repeated. Neither of the readings when repeated agreed with the previous readings. Repeat measurements

DIAGRAM II.



were made at room temperature, and these did not agree with the original measurements either. Finally repeat measurements were made in liquid hydrogen. The results were plotted for both the alloys (1.88 and 5.19) and we found that for each alloy there were two curves. The curves are shown in Diagram II. We think the change in resistance is due to the cooling to very low temperatures—a sort of ageing effect has probably taken place. This is supported by work we have done on ageing cobalt and chromium, which showed that ageing had the effect practically of shifting the temperature-resistance curve

down in the direction of the resistance axis. In the case of the alloys here in question the approximately constant difference of resistance seems to exist only above the temperature of liquid air.

Repeat measurements were made on the alloy containing 1.19 per cent. cadmium, and when these were plotted the constant difference of resistance was again apparent. The measurement in hydrogen for this alloy was made after the measurement in the helium liquefier, so that the reading for the hydrogen temperature before the cooling to 7° K. is not known. Readings are given in the table in two columns under the headings "after" and "before"—*i. e.* after the alloy had been in the liquefier and before. No "after" readings are available for the 0.127 per cent. and 2.76 per cent. alloys, as these resistances had been taken off the piece of fibre before this ageing phenomenon had been observed.

We do not wish to press any conclusion as we should first like to investigate much more thoroughly this strange ageing phenomenon. New questions at once arise; for instance, what temperature is necessary for the effect to take place? or, has time any influence on the ageing? or again, will cooling a second time to the superconducting temperature produce a further change? Until such questions be answered it is premature to say whether the effect is due to a separation of a solid solution into components or merely to some alterations in crystal structure. At all events, since a cadmium-lead alloy containing as much as 5 per cent. of cadmium was found to be superconducting, it is highly probable that there is a continuous chain of lead atoms in the superconducting state of the alloy.

LXVI. *Experimental Evidence of the Existence of Aggregates of Active Deposit Atoms in Gases containing Radon.* By Prof. E. L. HARRINGTON, *Ph.D.*, University of Saskatchewan, Canada*.

[Plate VII.]

Mlle C. CHAMIÉ† recently described experiments giving photographic evidence that radioactive material of various kinds when introduced into mercury exists in the form of aggregates rather than as individual atoms, regardless

* Communicated by Sir E. Rutherford, O.M., P.R.S.

† Mlle C. Chamié, *C. R.* clxxxiv. p. 1243 (1927).

of the method employed in activating the mercury. Later experiments* definitely indicated that these aggregates were in general not due to the association of radioactive atoms within the mercury, at least not solely, but actually existed as such before the introduction of the radioactive material into the mercury. In these experiments the aggregates were obtained from surfaces exposed to emanations and from surfaces activated in various solutions. From both theoretical and practical standpoints it is important to know whether in the case of surfaces exposed to emanations the aggregates form in the body of the gas and are deposited as such, or whether the process of aggregation takes place with atoms deposited individually on the surface exposed.

Certain work by Mme Curie †, by Makower and Russ ‡, and a number of others point definitely to the former process, though the latter may also function. This report has to deal with a somewhat different line of experimental investigation of this problem.

Experimental Methods and Results.

Since Mme Curie's work indicated a part played by gravity in the distribution of the active deposits on surfaces exposed to emanations, it was believed that by centrifuging tubes containing radon the distribution of active deposit on the walls should be affected. The experimental arrangement for measuring the distribution is indicated in fig. 1. Air-radon § mixtures were introduced into tubes such as T, and the latter mounted in such a way as to be adjustable in position along a vertical guide S provided with a scale. Two lead blocks LL situated between this guide and a gamma ray electroscope E were separated by a space of 1 cm., thereby forming virtually a slit. This limited the gamma radiation reaching the electroscope to that due to the portion of the tube immediately in front of the opening. The rate of fall of the electroscope leaf over a certain range of the telescope scale was taken as the relative activity of that portion of the tube in front of the slit.

Curve A of fig. 2 shows as a typical case the distribution of activity along a tube enclosing an air-radon mixture at atmospheric pressure, and containing 15 millicuries of radon.

* *Id.*, *ibid.* clxxxv. pp. 770, 1277 (1927).

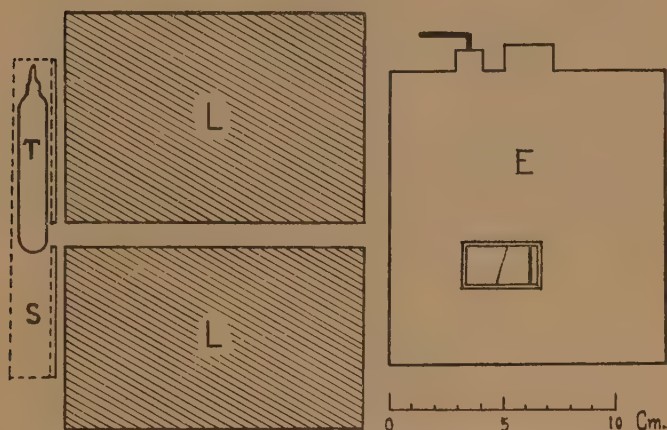
† Curie, *Radioactivité*.

‡ Makower and Russ, *Phil. Mag.* xix. p. 100 (1910).

§ The writer is indebted to Mr. G. R. Crowe for assistance rendered in connexion with the radon supply.

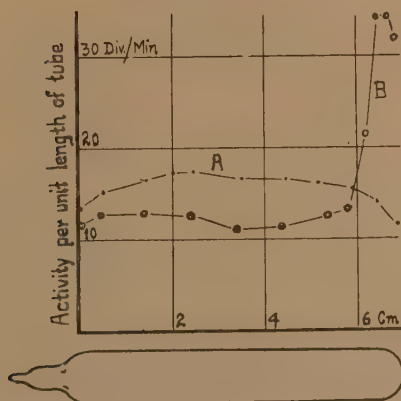
The ordinate at any point indicates the activity per unit. of length of the corresponding portion of the tube. After determining the activity distribution in the tube it was

Fig. 1.



Experimental arrangement for determining the distribution of activity along a tube.

Fig. 2.



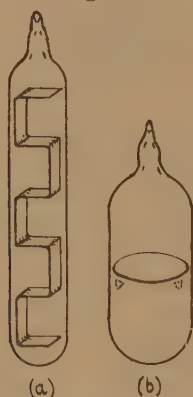
Curves showing the effect of centrifuging on the distribution of activity along a tube.

placed in a motor centrifuge (rounded end of the tube pointing outward) and centrifuged at about 1750 revolutions per minute for a period usually of the order of 30 minutes.

Since the circle described by the outer end of the tube had a radius of 15 cm., the centrifugal force acting on the particles near the end of the tube was about 500 times that exerted by gravity on the same particles. In view of the short mean life of some of the products, the advantage of this method over one depending on gravity is obvious.

Curve B of fig. 2, representing data taken immediately after the centrifuging, indicates the definite change in distribution caused thereby, obviously due to active material being thrown to the outer end of the tube. The magnitudes of the effects produced by centrifuging varied from unobservable ones to effects considerably greater than that shown in fig. 2. They increase with the partial

Fig. 3.



Tubes used to show that aggregates exist in suspension in the body of the gas containing radon.

pressures of radon and of water-vapour and with the total pressure, and depend somewhat on the shape of the tube. It is of interest to note that Mme Curie found a similar dependence on these factors in her work on the effect of gravity.

It is likely that in all cases a part of the effect of centrifuging is due to aggregates loosely attached to the wall being dislodged and thrown to the outer end of the tube. But the fact that the filter through which the radon mixture is removed always shows some activity, and the results shown by the following experiment, indicate that a definite portion of the material affected must come from the body of the gas. A strip of brass about 5 mm. wide was bent and inserted into a tube as indicated in fig. 3 (a); the

horizontal portions of the strip, or the "steps" of the "ladder," effectually divide the length of the tube into such short sections that any material dislodged from the walls of the tube during centrifuging would be unlikely to reach the middle portions of the steps. In one case the tube was centrifuged during the entire time (45 minutes) the radon-air mixture was in the tube, and in another case the radon was left in the tube overnight before centrifuging. In each case after removing the radon the tube was opened and the middle portions of the steps were cut out and laid on a photographic plate—the first step with the upper face up, the next with the upper face down, the next up, and so on alternately until the steps were all lying side by side in a row on the plate. This was then covered by another sensitive plate and left for about 10 minutes. On development each plate showed a row of alternately darker and lighter spots, and in every case the darker spots were due to exposure to the upper faces of the steps, *i. e.* to the faces pointing towards the axis of rotation of the centrifuge. On repeating the experiment but omitting the centrifuging, spots of uniform density were obtained.

The tube shown in fig. 3 (*b*) was used in a further test of the same sort. Here the tube was divided by a circular mica partition. After the centrifuging and removal of the radon the mica was placed on one photographic plate and covered by another. The results showed the upper face to have received the greater deposit. Fig. 4 (Pl. VII.) shows a greatly enlarged view of a portion of the plate exposed to the upper face, and indicates that in addition to a general distribution the active material is collected in aggregates distributed at random.

These experiments pointed definitely to the conclusion that the aggregates existed in suspension in the gas, and the size of these atomic groups, as suggested by their photographic action, indicated the probability of seeing them ultramicroscopically. Mme Curie (*l. c.*) and others have indeed reported having observed very persisting clouds in chambers containing gases including emanations and water-vapour. For a test of this a small brass chamber was constructed and filled with a radon-air mixture, and then examined ultramicroscopically by an arrangement similar to that described by Whytlaw-Gray*. Intense illumination, carefully adjusted, was required to make the particles visible, when they appeared as tiny "stars" exhibiting

* Whytlaw-Gray, Proc. Roy. Soc. cii. p. 600 (1913).

Brownian movements and drifting with the convection currents. An electric field, established between the central wire and the brass case by connexions to the D.C. mains, quickly swept the particles to one side. Even when the field had been left on for some time, only a comparatively short time, say 10 or 15 minutes, was required to elapse before particles again began to appear in the field of the microscope. The variations in the intensities of the "stars" and their activities in Brownian movements suggested a certain variation in their sizes. The particles visible in a freshly-filled chamber seemed to have higher mobilities than those visible later, but, except at first, little change with time was noticeable. This is due no doubt to the attainment of a condition of equilibrium in which the particles seen range in size from the smallest visible to the largest permitted by gravity to remain in suspension, new aggregates forming and growing and old ones disappearing owing to gravity or diffusion. Work along this line is being continued.

The question as to whether the particles detected ultra-microscopically are aggregates of radioactive atoms or merely dust requires consideration. In the first chamber used the radon-air mixture introduced had been previously used in a number of experiments like those described above, and this involved its being filtered a number of times through a cotton-wool plug; and it was again filtered as it was introduced into the brass chamber. Moreover, the application of the electric field should have disposed of any dust escaping all these filterings. However, the second chamber used was constructed as a miniature Wilson expansion chamber. It contained some water and was filled with filtered air only. Attempts to see particles were all unsuccessful; but when this same chamber was filled with a radon-air mixture similarly filtered, the particles were visible at once. Neither repeated expansions nor electric fields temporarily applied could permanently rid the field of particles, though such treatment should certainly have removed any dust. As further evidence on this point, it may be mentioned that, in some of the experiments on centrifuging first described above, the same tube, remaining hermetically sealed, was used on successive days without any apparent change in the definiteness of the effect produced by centrifuging.

The above experimental results are entirely in agreement with the experimental evidence obtained by others, and all considered together leave little doubt as to the actual existence of aggregates of radioactive atoms in suspension

in gases containing emanation. Certain other experiments, of which the details are considered unessential, will be mentioned in connexion with the next section.

It was felt that photographic evidence of these aggregates, obtained by methods similar to those described by Chamié (*l. c.*) or by Mühlestein* would be useful. The sensitive plates were "infected" in the following manner. As soon after the removal of the radon mixture as convenient the tubes were opened and the inner surfaces rubbed by a wire or a small steel ball mounted on a wire. The latter, bearing a certain amount of loosely adhering active material, was then tapped on the plates. These, on being developed, indicated that the spots of the gelatine actually touched became heavily infected, but there was also a scattering of independent and well-separated aggregates obtained elsewhere on the plate. Slow plates and slow development were found best. Fig. 5 (Pl. VII.) is a microphotograph showing the random distribution of aggregates thus obtained on the plates. Figs. 6 and 7 (Pl. VII.) show individual haloes at a still greater magnification. The "radiant" appearance is due to individual alpha particles from the aggregate passing through the air for different distances before striking the gelatine layer. When by a suitable arrangement a layer of mercury was left on the plate during exposure, all alpha particles except those having paths wholly within the gelatine were absorbed. The tracks of the alpha particles thus obtained are substantially equal in length, and define a circle having a radius equal to the range in gelatine of the alpha particles involved. Figs. 8 and 9 (Pl. VII.) show different magnifications of the circles thus obtained. Measurements on one hundred different diameters and involving many different circles and plates gave a mean value of approximately 53 microns as the actual radius of the circles on the original plates. Any plate will in general show circles having wide variations in the number of tracks radiating from the centres, some with only a few isolated tracks and others with so many as to make a solid black circle. The numbers of atoms in the aggregates must vary similarly, but the actual sizes of the aggregates are in general much too small to affect appreciably the diameters of the circles obtained.

Discussion.

The tendency of radioactive atoms to form aggregates was observed early in the course of experimental study by

* Mühlestein, *Archives des Sciences*, 5th, iv. p. 38 (1922).

different observers*. As to whether in the case of emanations this aggregation took place in the body of the gas or on the surfaces exposed to the emanations seemed less certain. No doubt existed as to the presence of the active deposit atoms in the gas containing the emanation, and in the light of the results obtained by others together with those described above. The obvious conclusion would seem to be that these atoms exist, at least in part, in the form of aggregates in suspension in the body of the gas.

Evidence as to the nature of the particles is more indirect, but yet suggestive. The importance of the presence of water-vapour raises the question as to whether the particles observed are minute drops of water incorporating a load of radioactive atoms or whether they are aggregates of the latter, including or absorbing water-vapour molecules to an extent determined by the partial pressure of the water-vapour. Those who have held the former view as to their nature have had to assume the presence of chemical compounds of some sort, say nitrogen oxides due to the action of the emanation on the air, in order to account for the persistence of these drops in an unsaturated atmosphere. But Mme Curie† was able to observe the gravity effect also in carbon dioxide and in hydrogen, and the present writer, in the course of experiments on centrifuging gases containing radon, substituted argon for air in certain cases without any observable change in the nature of results. This would seem to preclude the probability of any chemical action being essential to the formation of the particles. Vapour-pressure considerations would scarcely support the idea of the formation of minute drops of water in a non-saturated atmosphere in the absence of chemical compounds of some sort‡. That the effect persists even at very low vapour-pressures was seen from the following test. A tube containing the usual radon-air mixture with saturated water-vapour and also giving a marked effect of centrifuging was mounted with its lower end dipping 1 centimetre into a mixture of ether and carbon dioxide snow during the period of attaining equilibrium. The distribution of activity along the tube was then determined, after which it was returned to its former position long enough to offset the effect of any rise of temperature occurring during the taking of the observations.

* For detailed references consult Curie, *Radioactivité*; Rutherford, 'Radioactive Substances and their Radiations'; or Meyer and Schweidler, *Radioaktivität*.

† Mme Curie, *Radioactivité*, vol. i. p. 371, figs.

‡ See Poynting and Thomson, 'Properties of Matter,' 2nd ed. p. 166.

It was then centrifuged and again tested with the usual positive indication of active material having been thrown to the outer end. A second trial with argon substituted for the air gave like results. The vapour-pressure in these cases was certainly much too low to permit the formation of drops, and any excess water was frozen to the bottom of the tube before the tube was centrifuged. In the ultramicroscopic study mentioned above the observed particles were removed by an electric field temporarily applied, and from the vapour-pressure considerations referred to above one would expect that if any later condensation takes place it would be on the water surfaces already formed. It would appear then most unlikely that the new particles that appeared later were drops of water. Furthermore, Rutherford and others have found that for the greater part the active deposits carry positive charges. It is known from observations made with the Wilson expansion chambers that drops of water form more readily on dust particles or on negative ions than on positive ions, and in these experiments there could have been no shortage of available negative ions. These and certain other considerations have led the writer to the conclusion that the particles observed in non-saturated gases containing radon are not drops of water, but are aggregates of active deposit atoms. In saturated atmospheres no doubt both types of particle may exist.

The Origin of the Aggregates.

It would appear that particles might originate in either or in both of two ways. In the first place, the photographic evidence clearly proves that these aggregates do exist on surfaces which have been exposed to emanation. Makower and Russ (*l. c.*) and Lawson*, among others, have definitely proved the reality of the "aggregate recoil"—in other words, that when a member of an aggregate of radioactive atoms, say on a plate, ejects an alpha particle in the direction of the plate, not only the parent atom, but the entire aggregate containing this atom, may be thrown from the plate by recoil. This, then, offers one way of accounting for the aggregates found in suspension in the gas.

It appears probable, however, that most of the aggregates are actually formed in the gas itself. In the experiments described above there were atoms of radon and of subsequent members of the series, molecules of air of water-vapour, and

* Lawson, *Wien. Ber.* cxxvii. p. 1315 (1918); cxxviii. p. 795 (1919).

of unknown other kinds present in the tubes employed. This mixture was subjected to the intense ionizing action of alpha, beta, and gamma rays and of recoil atoms, and there must have resulted a corresponding variety of ions, some positive, some negative. That atoms of active deposit generally carry positive charges has been repeatedly observed, and that a considerable number carry negative charges was indicated by the following test:—Three long narrow plates were mounted parallel to and symmetrically about the axis of a glass tube into which the usual radon-air mixture was introduced to a pressure nearly atmospheric. Two of these plates were connected to the terminals of a 200-volt D.C. line, and the third left insulated. After due exposure the plates were removed and placed on a photographic plate. The latter on being developed showed that the cathode had received a much heavier deposit than the anode, but that the anode had received a very definitely greater deposit than the third plate. Since, then, active deposit ions of unlike sign do exist, there must be combinations between them in addition to the many other kinds of combinations possible with such a variety of ions. If in any combination only molecules of gases are involved, these molecules should separate at once and be as independent as they are normally. But if the ions, whether simple or cluster ions, included two or more atoms of radioactive or other substance normally existing as a solid under the conditions of the experiment, there appears to be no obvious reasons why these should separate. On the contrary, every consideration indicates that they should remain together. Moreover, at least a certain proportion of the molecules of air, or especially of water-vapour, included in the uniting ions would be expected to remain in the resulting group or particle because of the tendency of such molecules to become absorbed on solids. Therefore in such a mixture of ions the probability of combinations of permanent nature is very high. Once a nucleus of an aggregate is formed, the chance of further acquisitions increases with the growth of the aggregate, since its mobility and therefore its chance of reaching the wall must decrease, and its probability of being struck by other particles or molecules must increase with its size. This growth should continue until it is removed by diffusion, by electric field, or by gravity.

Whether the aggregates known to exist on the surfaces exposed to emanations originate thus or actually form on the wall will not be discussed here; but this theory would explain the experimentally observed fact that these aggre-

gates are, at least in many cases, but loosely attached to the activated surface.

On this theory the rate of growth of an aggregate would increase with the number of atoms of active deposit, of molecules of vapours, and of any other substance not able to leave a combination once formed. These deductions appear to fit known experimental facts, and in particular to explain the part water-vapour may play, even in a non-saturated atmosphere, in the formation of these aggregates.

Summary.

Experimental evidence is given of the existence of aggregates of atoms of active deposit in mixtures of radon and air, also of radon and argon, including in either case more or less water-vapour. The evidence is both direct and indirect. Photographic evidence as to the nature and variety of these aggregates is included.

Suggestions as to the possible origin of these aggregates seem to account for the facts experimentally obtained by various observers.

The writer is grateful to the University of Saskatchewan for the grant of a leave of absence, and particularly indebted to Professor Sir Ernest Rutherford for his kindness in granting him the privilege of working in the Cavendish Laboratory, for suggesting the problem, and for his interest and many suggestions during the course of the work. He would acknowledge also the valuable assistance given by Dr. Chadwick, who had much to do with providing the facilities and materials required.

Cavendish Laboratory,
June 23, 1928.

LXVII. *Molecular Cohesion.* By G. A. TOMLINSON, B.Sc.*

[Plate VIII.]

(1) **T**HE amount of well-established knowledge concerning the nature and origin of interatomic forces is very limited. Within recent years the theoretical aspect of the question has received much attention, and a number of interesting and suggestive results have been obtained by mathematical methods. It is generally agreed, however, that the problem of atomic forces has not been solved, and

* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

even on the more restricted question of the relation between the force and the distance, different workers are not at all in agreement. It is known that atoms or molecules in any of the states of matter can exert a powerful attraction on one another when very close together, and there is reason to believe that the effective field of the attraction force is at the most only a small multiple of the dimensions of the molecule. Thus in liquids the force becomes negligible at distances of the order eight times the normal distance between the molecules.

For equilibrium to exist among the atoms of a solid, we are compelled to suppose that the atoms also exert a repulsive force on each other, a force about which there appears to be hardly any positive knowledge, except that the sum of the repulsive forces must be in balance with the sum of the attractive forces. There is reason to think that the repulsion falls off at a considerably greater rate than the attraction as two atoms separate, and therefore has a smaller field. Simple considerations of the stability of the atoms in the solid require this to be so.

Several distinct atomic attractive forces must be recognized, such as the force of chemical affinity, the binding force in polyatomic molecules, and the cohesive attraction exerted generally by all atoms or molecules. The cohesive force is some rapidly diminishing inverse function of the distance between the atoms, and very varied suggestions have been made as to the probable law of force. Many years ago, Sutherland* gave reasons for believing that gaseous and liquid molecules attract according to an inverse fourth-power law. He also published a kinetic theory of solids† in which the same law is assumed. Chatley‡ has suggested that the attraction in the case of solids follows an inverse sixth-power law. Järvinen§ considers that molecules attract according to a law, force $\frac{m^2}{d^5}$, in which m is

the mass of the molecule. Kam|| arrives at a conclusion favouring an inverse square law, and Antonoff¶ from surface-tension phenomena suggests an inverse fourth power. Lennard-Jones** finds for the inert gases that the most probable index is -5 . In his Cantor lectures on the

* Phil. Mag. xxiy. and xxvii. (1889).

† Phil. Mag. xxxi. (1891).

‡ Proc. Phys. Soc. xxvii.

§ Zeit. Phys. Chem. 1914.

|| Phil. Mag. xxxvii.

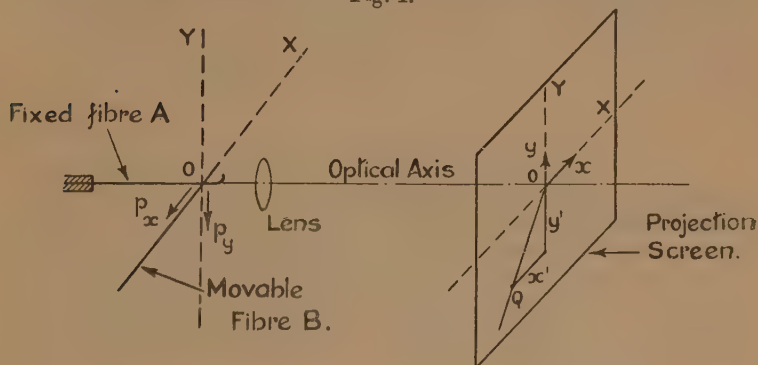
¶ Phil. Mag. xxxvi.

** Proc. Roy. Soc. cxii.

structure of metals, Rosenhain* mentions an inverse cube law as a probable description of the forces between metallic atoms. Finally, Edser† has suggested that it is necessary to consider a higher index than any of those already mentioned, and regards -8 as being more probable.

(2) The present paper gives a description of some experiments in which the force of adhesion between fibres and spheres of glass or quartz can be observed and measured. The results obtained experimentally are then compared with those to be expected by calculation, if the molecular attraction follows a law $F = Kd^{-n}$, different integral values being allotted to the index n . There is no very strong *a priori* reason for thinking that the force between two atoms can be described by a simple inverse law, such as the above, in which

Fig. 1.



n is an integer; but, on the other hand, as the above references show, there is such diversity of opinion as to the approximate law of force, indices of 2, 3, 4, 5, 6, and 8 being suggested by different writers, that any evidence in support of a particular integral index may be considered to be a small advance in our knowledge of the nature of the attraction.

If two freshly-drawn fibres of glass or quartz are brought into contact, they are found to adhere, and, on separating the fibres, the force of adhesion causes a measurable elastic deflexion of the fibres. Similarly, the force of adhesion of two fused spheres can be observed if the spheres are flexibly supported, as, for example, by a piece of piano wire. Measurements of the force were made in the following way. One fibre, A (see fig. 1), was supported as a cantilever in a

* Cantor Lectures, 1925.

† Brit. Ass. Rep. 1922.

horizontal optical projector, its direction coinciding with the optical axis. The tip of the free end of the fibre was bent upwards and was focussed at the screen. A second fibre, B, was held below the first at right angles to it, and this fibre could be moved in two directions, OX and OY, at right angles. The two fibres were brought into contact, when they adhered, and then they were drawn apart until they separated. The deflexion of the fixed fibre at the point of separation was marked on the screen, from which the force of adhesion can be found by calibrating the stiffness of the fibre with light wire riders.

The fixed fibre A can be deflected either downwards in the direction OY by a force normal to the contact surfaces, or horizontally along OX by a tangential frictional force. If the measured deflexions of the fixed fibres in the two cases are y and x , and λ denotes the stiffness of the fibres in dynes per cm. deflexion and μ is the coefficient of friction between the fibres, then the force of adhesion in the two cases is

$$p_x = \frac{\lambda x}{\mu},$$

$$p_y = \lambda y.$$

The first case may be called free adhesion, since the normal force between the fibres is solely that due to adhesion, no external normal force being applied. The second case may be called the limiting adhesion when the fibres are separated. It was always found that p_x was considerably greater than p_y . A typical example of adhesion measurement is given below.

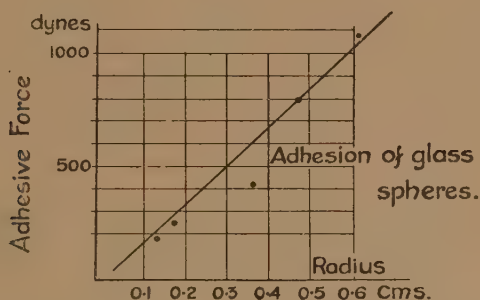
Material	drawn quartz fibres.
Radius	0.006 cm.
Stiffness	= 3.33 dynes per cm.
Deflexion	$y = 0.204$ cm.
	(mean of 78 readings).
„	$x = 0.52$ cm.
	(mean of 61 readings).
Coefficient of friction	0.58.
Free adhesion force	$p_x = 2.98$ dynes.
Limiting adhesion force ...	$p_y^* = 0.68$ dynes.
Ratio	$\frac{p_x}{p_y} = 4.4.$

The coefficient of friction was determined by mounting two much stiffer fibres in the same way. The fibres were

pressed together by a normal force which was found from the deflexion y' of the fibre (fig. 1). The fixed fibre was then pulled tangentially through a distance x' until slipping occurred. A group of such points was obtained and a mean line, OQ, was drawn through them. From the slope of this line the coefficient was found. The fibres used were freshly drawn and comparable in every way, except as regards diameter, with those used in the adhesion measurements, so that the value of μ is probably closely the same in both cases. Stiff fibres were used to ensure that the applied force was far larger than the forces concerned in adhesion.

Some further experiments were made in which the limiting adhesion (p_y) was measured for freshly-blown glass spheres of various radii. Some results obtained, each being the mean of a considerable number of observations, are shown in fig. 2.

Fig. 2.



The curve indicates that the adhesion force is proportional to the radius of the sphere. The observations do not fall very exactly on the mean straight line, but, having in view the nature of the measurements, there appears to be sufficient consistency to support the conclusion that the relation is linear. With the spheres, quite large adhesion forces are observed. Thus with the largest spheres of 1.22 cm. diameter the force slightly exceeds 1 gm. weight.

(3) Before considering the experimental results further, the cause of the observed force will be discussed shortly. It is necessary to establish securely that the force is one of molecular cohesion. It is possible that a force similar to that observed might be due to electrification. This has been tested by discharging any electrification by strong ionization with radium both before the fibres touch and also while adhering together with a force applied tending to separate

them. The ionization was found to have no effect on the force. Another possible cause is the presence of an adsorbed film of liquid. Against this must be placed the fact that the force exerted by the fibres is always found to be at its strongest just after they have been cleaned by heating to a bright red in a flame. The force is found to diminish slowly with time, and in making the measurements the fibres were actually repeatedly re-heated. The magnitude of the measured forces also appears to be altogether too large for an explanation depending on the surface tension of a liquid film to be satisfactory.

More positive evidence that the force is due to cohesion can be obtained by examining the surface of glass that has been in contact. Fig. 3 (Pl. VIII.) shows an enlarged photograph of a piece of clean glass plate which has been very lightly stroked with a fused glass sphere. It will be seen that, as the sphere moves, a succession of flakes have been torn out of the plate, and at each tear the sphere jumps a short distance clear of the plate, its track being clearly shown as a broken line. A similar effect has been described by Hardy in his work on lubrication. This experiment conclusively shows that strong cohesion occurs at the contact.

(4) The experiment with the adhering fibres will next be considered in some detail, as facts of some interest can be deduced from the results. In the condition of free adhesion the attraction between the fibres results in a normal pressure, $p_x = 2.98$ dynes, which will produce a small elastic indentation, the contact area being a circle the radius of which is 3.4×10^{-5} cm., calculated by the usual equation of Hertz. In the second case of limiting adhesion the force exerted is 0.68 dyne, and there is no residual pressure reaction between the fibres, which are just on the point of separating and are in a purely geometrical contact. The last statement can be substantiated experimentally by observing the behaviour of the fibres as they approach each other. It is found that the fibres adhere quite suddenly without any external pressure being applied, which is shown by the absence of any deflexion of the fixed fibre. There is no doubt that adhesion has occurred, as the minute vibrations of the fibre are immediately checked, and, further, if the movable fibre is now withdrawn, it draws the fixed fibre with it. Hence the molecular attractions acting at the instant of geometrical contact are sufficient to draw the fibres together into the condition of complete free adhesion.

A similar conclusion is reached by reasoning from the equilibrium of the two fibres. In general, three forces are acting: (a) an external separating force F ; (b) an elastic reaction, the sum of a large number of molecular repulsions $\Sigma(R)$; and (c) a cohesive attraction, the sum of a large number of molecular attractions $\Sigma(A)$.

For equilibrium we must have

$$F + \Sigma(R) = \Sigma(A).$$

The bodies are in equilibrium for all values of F from zero in free adhesion to p_y , the limiting normal force, since F can be continuously increased in the experiment from zero upwards. Hence, if a small increment dF of the external force produces a relative displacement of the fibres of amount dx , we must have

$$\begin{aligned} dF + d\Sigma(R) - d\Sigma(A) &= 0 \\ \text{or} \quad \frac{dF}{dx} &= \frac{d\Sigma(A)}{dx} - \frac{d\Sigma(R)}{dx}. \end{aligned}$$

Since the attractive and repulsive forces must both diminish to zero with increasing distance between the bodies, $\frac{d\Sigma(A)}{dx}$ and $\frac{d\Sigma(R)}{dx}$ are essentially of opposite sign to $\frac{dF}{dx}$, and it follows, therefore, that for all positions of equilibrium $\frac{d\Sigma(R)}{dx}$ must be numerically greater than $\frac{d\Sigma(A)}{dx}$.

Initially, in free adhesion, $\Sigma(R)$ and $\Sigma(A)$ are equal; hence the above considerations lead us to expect that $\Sigma(R)$ will continuously decrease relative to $\Sigma(A)$ as the fibre is steadily deflected, until finally $\Sigma(R)$ approaches zero and $\Sigma(A)$ has the limiting value p_y as measured, after which the fibres separate.

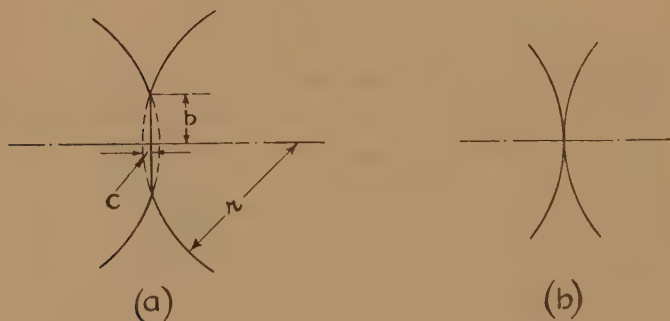
The experiment thus demonstrates that the molecules of a solid exert a cohesive attraction through space on other molecules. Actual contact is not necessary for cohesion to be operative, defining contact as the approach of the molecules sufficiently near to give rise to a repulsive reaction force. It is interesting to find this direct experimental evidence that the molecule of a solid thus possesses a certain small field of attraction, such as matter in the liquid and gaseous states is known to possess.

The experiment further appears to throw a little light on the nature of the repulsion force between molecules. Present conceptions of the structure of the atom compel us to

postulate the existence of a repulsion field, and a number of workers in mathematical physics arrive at the conclusion that this repulsion field falls off much more rapidly than the cohesive attraction field. The behaviour of the fibres described above appears to furnish some direct experimental evidence that the repulsion certainly has this property, although no quantitative information can be derived about the relative rates of change of the attraction and repulsion. However, since practically nothing is known at present about the atomic repulsion, it would appear that any knowledge, however slight, that is based on experimental observations is worthy of note.

Some information of a qualitative kind can be derived from the experiment as to the range of the field of attraction. For this purpose it is convenient in imagination to

Fig. 4.



substitute two spheres of twice the radius of the fibres for the two crossed cylinders, the two cases being identical as regards mean curvature over the small region concerned around the point of contact. Fig. 4 then shows the condition of the two bodies (a) in free adhesion and (b) in geometrical contact as in limiting adhesion. The exact form taken by the bodies in case (a) is unknown, but by making the simple assumption that the deformation takes the form of a small circular flat of radius $b = 3.4 \times 10^{-5}$ cm., the dimension c in the figure is found to be 4.8×10^{-8} cm., which is comparable with atomic dimensions. The force of adhesion in this case was found to be 4.4 times as great as the force in case (b), and the experiment thus gives a general indication of the rapidity with which the attraction diminishes as the distance separating the molecules is increased.

(5) An attempt will next be made to interpret the experimental results on the basis of a simple inverse law of molecular attraction

$$\text{Force} = \frac{K}{d^n}$$

with a view to finding what integral value of n is in best agreement with the results.

It is not possible to calculate the force of adhesion between the fibres in either of the cases, but we can calculate the ratio of the forces by making certain assumptions, and this ratio, assigning different possible values to n , can be compared with the ratio 4.4 found experimentally.

We shall first attempt to show that there is a lower limit to the possible values of n , this limit being 4 if cohesive attraction is supposed to reside in the surface molecules, and 6 if all the molecules of the two bodies are exerting attractions similar to gravitating particles. The first of these alternatives appears to be the more probable, and conforms with the present view held by many, that cohesion is an electrical force accompanying the structure of the atom, adhesion being due to the cohesion fields of the unsymmetrical surface molecules.

In order to derive an expression in a simple way for the total force of attraction between the fibres, we shall substitute for the crossed fibres a plane and a sphere of the same radius as the cylinders. This artifice is justified by the knowledge that the effective force is confined to those atoms in a small region round the contact, of dimensions comparable with molecular dimensions, and the sphere and plane are identical as regards mean effective curvature with the crossed cylinders. We shall in the first place determine the adhesion force with the sphere and plane in geometrical contact, on the assumption that only the surface molecules exert cohesive attraction.

It is necessary in the first place to determine the force exerted normal to its surface by a plane on a single molecule at a distance a from the surface. Let e be the mean distance between the molecules. Then we may either find the total attraction on the single molecule by infinitesimal methods, taking the source of attraction as being continuous over the surface or throughout the body, or we may find the arithmetical sum of the separate attractions treating each molecule as a discrete point for this purpose.

The integration method strictly is not correctly applicable, since it is known in advance that a is of the same order as e ,

but the result is more useful being in algebraic form, and it has been found by actual trial to differ only very little from that obtained by the arithmetical summation.

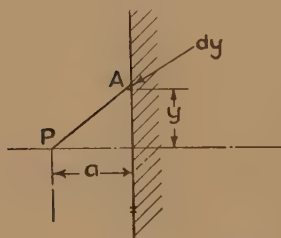
Taking firstly a surface distribution of attracting matter, let s be the number of molecules per unit area. In fig. 5 let P be the position of the external molecule, then the normal attraction of a ring element of the surface of radius y is

$$\frac{2\pi K s y dy}{(PA)^n} \times \frac{a}{PA},$$

and the attraction of the whole surface is

$$F = 2\pi K s a \int_0^\infty \frac{y \cdot dy}{(a^2 + y^2)^{\frac{n+1}{2}}} \dots \dots \dots (1)$$

Fig. 5.



Making the substitution $y = a \tan \theta$, this becomes

$$F = \frac{2\pi K s}{a^{n-2}} \int_0^{\pi/2} \sin \theta \cos^{n-2} \theta d\theta \dots \dots \dots (2)$$

The definite integral is a pure number which will be denoted β .

The attraction between the plane and the sphere can now be found by dividing the spherical surface into elements parallel to the plane and at a distance x from it, having a width dx measured along the common normal.

The normal attraction to the plane of an element, by equation (2), is

$$\frac{2\pi K s \beta}{x^{n-2}} \times 2\pi s r dx,$$

or the total attraction is

$$4\pi^2 s^2 K \beta r \cdot \int_e^{me} \frac{dx}{x^{n-2}} \dots \dots \dots (3)$$

It may be postulated that two molecules at the point of geometrical contact cannot be closer together than two molecules are in the interior of the solid. The value of the lower limit is therefore taken to be e .

The attraction between two molecules falls off so rapidly with increasing distance that the integration need only extend over a small cap of the sphere, and the upper limit has been written as a multiple of e where me is small compared with r , but is sufficiently large compared with e itself. Equation (3) shows that no integral value of n less than 4 is admissible. It is necessary, to be consistent with what is known experimentally about adhesion, that the integral should be zero at the upper limit. For values of n less than 4 this is not the case, and we should arrive at the result that the adhesive force at the contact was a function of the dimensions of the body other than the curvature at the point of contact.

The total attraction between the sphere and plane will next be found on the second assumption, namely that all the molecules of the body exert attractive forces.

As before, we shall first find the attraction of the plane body on a single molecule at a distance a from the surface by dividing the body into plane elements of thickness dx at a distance x from the single molecule.

Then, by equation (2), the attraction of any element is

$$\frac{2\pi K\beta S dx}{x^{n-2}},$$

where S is now the number of molecules in unit volume. The whole attraction on the molecule is then

$$2\pi K\beta S \int_a^\infty \frac{dx}{x^{n-2}} = \frac{2\pi K\beta S}{n-3} \times \frac{1}{a^{n-3}}, \quad (4)$$

and the total attraction of the sphere and plane body is

$$\frac{2\pi K\beta S}{n-3} \int_e^{me} \frac{\pi y^2 S dx}{x^{n-3}}.$$

As we are concerned only with a small region near the point of contact, we may put

$$y^2 = 2rx,$$

and the attraction becomes

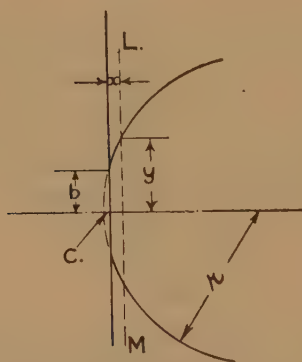
$$\frac{4\pi^2 S^2 K\beta r}{n-3} \int_e^{me} \frac{dx}{x^{n-4}} \quad \dots \quad (5)$$

In this case, for similar reasons, no integral value of n less than 6 can be accepted.

(6) We shall next take the experimental result that the ratio $\frac{p_x}{p_y} = 4.4$, and compare this with the values that can be computed for this ratio on assigning various values to the index n . Dealing firstly with the case in which cohesion is assumed to be a surface phenomenon, the force of free adhesion, as in fig. 6, may be divided into two parts: p_1 for the circular area of contact of radius b , and p_2 for the remainder of the sphere.

It can be shown that p_2 is independent of b , the radius of the contact circle, when b is small compared with the radius

Fig. 6.



of the sphere. If any plane section is taken, such as LM in fig. 6, of radius y , the area of the spherical cap is

$$A = 2\pi r(c + x),$$

$$\text{or} \quad \frac{dA}{dx} = 2\pi r.$$

The attraction on any ring element of the surface is a function of the area of the element and the distance x whatever the law of attraction may be. Between any values x and $x + \delta x$ there is a constant increment of area independent of the value of y . Hence the total attraction is independent of the value of b . It therefore follows that p_2 is equal to p_y , the total attraction occurring in the case of limiting adhesion of fig. 4 (b), which corresponds to the

particular case of $b=0$; and this has already been found by equation (3) to be

$$p_2 = p_y = 4\pi^2 s^2 K r \beta \frac{1}{(n-3)e^{n-3}} \dots \dots (6)$$

To find the value of p_1 , let it be assumed that the atoms in contact are separated by a mean distance e . Then, neglecting a small edge effect, the adhesion of these surfaces can be found from equation (2), and is

$$p_1 = \frac{4\pi^2 s^2 K \beta b^2}{2e^{n-2}} \dots \dots \dots (7)$$

Hence
$$\frac{p_1 + p_2}{p_2} = \frac{p_x}{p_y} = 1 + \frac{(n-3)b^2}{2re} \dots \dots \dots (8)$$

In taking the ratio, all the unknown terms disappear, and if an average value such as 3×10^{-8} cm. is assumed for e , the ratio can be found for various assumed values of n as given below :—

n	2	3	4	5	6	7	8
$\frac{p_x}{p_y}$	-2.2	1	4.2	7.4	10.6	13.8	17.0

The value of n yielding a result nearest to that found by experiment is 4. It is of interest to note that both the table and the form of equation (8) again show that no index under 4 can possibly give a result in agreement with experiment, an index 3, for example, giving $p_x = p_y$ whatever the values of b and r may be. The rate of variation of p_x/p_y with n is unfortunately not large enough, for values of n greater than 3, to say with any finality that an index exceeding 4 is also not possible, but it may be said that 4 is the most probable value.

If a similar calculation is made on the second assumption that all the molecules throughout the solid are effective in causing adhesion, the following result is obtained :—

$$\frac{p_1 + p_2}{p_2} = \frac{p_x}{p_y} = 1 + \frac{n-5}{n-4} \times \frac{b^2}{2re}, \dots \dots (9)$$

and this gives numerical values as below :—

n	4	5	6	7	8	9
$\frac{p_x}{p_y}$	—	1	2.6	3.13	3.4	3.56

These results are not very conclusive for values of n over 5, but, on the other hand, the assumed distribution of molecular forces is somewhat improbable, as already stated. Equation (9) indicates that 6 is the minimum value of n , which would be consistent with the experiments.

(7) Various workers in mathematical physics have advanced the conception that the atom behaves as an electric doublet when in close proximity to another atom. This view has been successfully applied to the theory of specific inductive capacity from which the electrical moment of the doublet has been calculated in certain cases. It is interesting to note that this conception leads at once to an inverse fourth-power law of attraction, and at the same time offers a partial explanation of the universal property of atoms to exert cohesion. If the doublet hypothesis is assumed to be correct, an interesting result is obtained on comparing some of the calculated electrical moments with the corresponding value found for glass, which may be derived from the present experiments on adhesion in the following manner. The constant K can be determined by assuming the attraction to follow an inverse fourth-power law on the doublet theory and as indicated, although somewhat indecisively, by the experiments described.

The force of attraction between two spheres of radius r can be derived from equation (3) above, and is

$$p_y = \frac{2\pi^2 s^2 K r}{3e}, \dots \dots \dots (10)$$

and in fig. 2 the measured adhesion of glass spheres is given. It may be noted that equation (10) shows that a linear relation should exist between the force and the radius, a result approximately found by experiment. From the curve in fig. 2 the mean value of $\frac{p_y}{r}$ is 1650; hence the constant K is given by

$$K = \frac{3e}{2\pi^2 s^2} = \frac{p_y}{r} = 250 \frac{e}{s^2}.$$

If we suppose the molecules to be closely packed hexagonally in the surface, each is at a distance e from its neighbours, and s has a value $\frac{2}{\sqrt{3}e^2}$. The particular type of arrangement assumed does not greatly affect the estimate of K , and this value of s will be assumed. Close packing in square

formation, for example, gives a value $1/e^2$ for s which differs only slightly from the above. Using the first value of s , we have

$$K = 187 e^5.$$

Assigning an approximate value 3×10^{-8} to e , the value of K is 0.45×10^{-35} . The force between two doublets of moment M at a distance x apart varies between $\frac{6M^2}{x^3}$ when end on and $\frac{3M^2}{x^4}$ when broadside on. If the force of cohesion follows a law

$$F = \frac{K}{x^4},$$

we shall have K varying from $6M^2$ to $3M^2$,

$$\text{or } M \text{ varying from } \sqrt{\frac{K}{6}} \text{ to } \sqrt{\frac{K}{3}}.$$

Taking the above value of K , we find M to lie between 1.22×10^{-18} and 0.86×10^{-18} .

Sir J. J. Thomson* gives the following values of the calculated electrical moment:—

$$M = 2.1 \times 10^{-18} \quad \text{for } H_2O,$$

$$M = 1.5 \times 10^{-18} \quad \text{for } NH_3.$$

These values are derived from measurements of the variation of the specific inductive capacity with temperature.

The agreement in the order of magnitude of the electrical moments is remarkable, and appears to justify the tentative suggestion that cohesion is perhaps the attraction of two molecular doublets. This view also lends support to the idea that only the surface atoms exert attraction on external atoms. The field of an interior atom, it is reasonable to suppose, is absorbed by a neighbouring atom, and only the unsymmetrical surface atoms have any appreciable field extending beyond the boundary of the body into space. The molecular theory of magnetization provides an analogy in this respect.

The electrical moment of a doublet is the product of a quantity and a length, and a doublet theory of atomic attraction would be quite untenable if this length should be found to exceed the known atomic dimensions. The quantity concerned in the product cannot be less than the electron

* 'The Electron in Chemistry,' p. 49.

charge q , and hence a maximum possible value $\frac{M}{q}$ can be calculated for the length of the doublet.

Taking the higher value 1.22×10^{-18} for M , this gives a maximum length of 0.2×10^{-8} cm., or about $1/15$ of the diameter of the atom, and the doublet theory thus involves no inconsistency with respect to the size of the atom.

(8) The probability that the cohesive attraction follows an inverse fourth-power law can be subjected to a further indirect test by calculating the tenacity of glass. For this purpose the tenacity will be considered as equivalent to the cohesive attraction, with an inverse fourth-power law, between two imaginary plane faces inside the material. The attraction of one plane for a single molecule of the other face can be obtained from equation (2), and is given by

$$\frac{2\pi Ks}{3e^2},$$

and the attraction of the faces per unit area is therefore

$$F = \frac{2\pi Ks^2}{3e^2}.$$

If, as before, a close packing of molecules is assumed and s has a value $\frac{2}{\sqrt{3e^2}}$, we have

$$F = \frac{8\pi K}{9e^6}. \quad . \quad . \quad . \quad . \quad . \quad (11)$$

An estimate of this in the case of glass, using the previous values of K and e , is

$$F = 1.7 \times 10^{10} \text{ dynes per sq. cm.}$$

This value is much greater, about twenty times, than the tenacity usually found for glass, but it is generally recognized that the actual tenacity of materials as found by tensile tests is always far short of the ideal tenacity which the cohesion forces would impart. Griffith*, however, has obtained some remarkably high tenacities for drawn glass fibres, and some of his results exceed the above amount, though generally this calculated tenacity is of the same order as Griffith's experimental results.

The mechanism of rupture in tension is so imperfectly understood at present, especially in crystalline materials

* Phil. Trans. ccxxi.

such as the metals, that it is hardly safe to base any conclusions on comparisons of actual and ideal tenacities. In the case of glass, which has an amorphous structure, this objection perhaps has less weight, as Griffith has clearly shown that tenacities approaching the ideal value can be actually realized. There is, however, an interesting relation in the case of metals which has not been mentioned previously as far as the writer is aware. Table I. gives the crystal lattice constant and the closest approach of the atoms for a group of seven metals, all of which crystallize in the face-centred cubic system. Values of $1/e^6$ are given in

TABLE I.

Metal.	Lattice constant.	Closest approach of atoms e .	$1/e^6$.	Tenacity f dynes per sq. cm.	Ratio $\frac{f}{1/e^6}$.
Nickel	3.54×10^{-8}	2.505×10^{-8}	40.5×10^{44}	5.3×10^9	0.131×10^{-35}
Copper	3.60	2.540	37.1	4.3	0.116
Platinum ...	3.92	2.780	21.6	3.3	0.152
Silver	4.06	2.876	17.65	2.9	0.164
Aluminium ..	4.05	2.860	18.3	2.3	0.126
Lead	4.92	3.480	1.78	0.21	0.118
Gold	4.08	2.880	17.55	2.3	0.131

column 4, and, as the table is purely comparative, e has been taken as the closest approach of the atoms. Together with these, the measured tenacities of the metals are given and the ratio of the tenacity to $1/e^6$.

It will be seen that this ratio is approximately constant for the series of metals, though the tenacities concerned cover a fairly wide range. It should be remarked that this relation is based entirely on experimental determinations of e and f . The relation appears to be definite enough to suggest that a rational basis underlies the empirical result. Some care must be exercised in attempting to interpret the result, as various considerations become involved. Thus, for example, if we suppose the expression of equation (11) to give the ideal tenacity, assuming the inverse fourth-power law of atomic attraction to hold, we obtain a rational

explanation of the index 6 in the relation $fe^6 = \text{constant}$, but only subject to two conditions, viz. that the measured tenacity is nearly the same fraction of the ideal tenacity, and that the cohesion constant K is nearly the same for all the metals concerned. The first of these is not an unreasonable supposition for a group of pure metals having identical crystal lattices. Nor is there any obvious intrinsic objection to the second condition, as the table itself shows that, with the high index 6 comparatively small, variations in the lattice constant can in themselves account for wide differences in tenacity without the necessity for supposing large variations in the atomic constant.

For the present it would be unsafe to say more than that the empirical relation is not opposed to the inverse fourth-power assumption, but as definite evidence in favour it can only be accepted with some reserve.

The author wishes to record his thanks to Sir Joseph Petavel, Director of the National Physical Laboratory, and to Mr. J. E. Sears, Superintendent of the Metrology Department, for their kind interest and encouragement.

1st August, 1928.

LXVIII. *The Reflexion of Electrons from an Aluminium Crystal.* By D. C. ROSE, Ph.D., 1851 Exhibition Senior Student*.

THE development of the new wave mechanics has recently directed considerable attention to experiments on the scattering of particles. One of the outstanding features of the theory is that it indicates that a particle of mass m may be treated as a wave-like disturbance of wavelength $\lambda = \frac{h\sqrt{1-\beta^2}}{mv_e}$, where v_e is the velocity of the particle,

or considering the particle as a wave, the velocity of propagation of energy. It is connected with the phase velocity v_p by the relation $v_e v_p = c^2$. This means that, if suitable conditions could be found, a beam of particles might be expected to have the properties of a ray of light.

If such is the case, the most obvious method of testing the theory is by looking for refraction or diffraction of

* Communicated by Sir E. Rutherford, P.R.S.

beams of particles by methods similar to those used in studying radiation of corresponding wave-length. The diffraction phenomenon would be expected to exist for α -particles, β -particles, electrons, positive ions, or such moving particles. The wave-length corresponding to an α -particle is of the order of 10^{-13} cm. and is therefore too short to be studied by ordinary methods. Similarly, owing to the high velocity of β -rays and the large mass of positive rays, the wave-lengths corresponding to these are in general too short to be measured easily. For an electron, however, the corresponding wave-length may be brought into the X-ray region by giving it a suitable velocity. The wave-length associated with a 100-volt electron is 1.2 Å. It would therefore be expected that the phenomenon of the diffraction of X-rays by a crystal grating might be observed with a beam of electrons. In the present paper an experiment is described in which a beam of electrons has been diffracted in an aluminium crystal in a manner similar to that used for the analysis of X-ray beams.

Two methods of studying such a beam of electrons are available. The first method corresponds to the Laue method of examining crystal structure by X-rays. As it is generally known, if a narrow beam of X-rays strikes a crystal face normally and the intensity of the scattered beam is measured in all directions, sharply defined diffracted beams occur whose direction is connected by a simple relation with the crystal structure, its orientation with respect to the incident beam and the wave-length. G. P. Thomson⁽¹⁾ showed that such diffracted beams could be found by passing a narrow beam of cathode rays through thin metal foils. Davisson and Germer⁽²⁾ have also performed such an experiment with electrons. They bombarded the face of a nickel crystal cut parallel to a (111) plane with a beam of electrons at normal incidence. As the electrons could not penetrate through the crystal, they could only examine the region on the same side of the crystal as the incident beam. Several diffracted beams of electrons were found which correspond to Laue beams. These did not occur exactly in the position calculated from the known structure of nickel and the wave-length corresponding to the beam of electrons. They could, however, be brought into agreement by assuming that the crystal was contracted somewhat in the direction of the incident beam. A more correct explanation seems to be the assumption of an index of refraction for these waves in the metal. This point will be discussed later.

The other method of studying the diffraction of electrons is analogous to the Bragg method of analysing a beam of X-rays. If a narrow beam of X-rays impinges on a crystal making an angle θ with one of the planes of the crystal structure, the rays scattered from successive planes one behind the other build up a sharp beam in the position of normal reflexion, also at an angle θ with the crystal plane. The wave-length and the angle θ are connected by the well known formula

$$n\lambda = 2d \sin \theta, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n is the number of wave-lengths in the path difference between rays from two successive planes in the crystal, or the order of the reflected beam, and d is the spacing between the planes.

In the experiments described here an attempt was made to obtain a reflected beam of electrons by replacing the X-ray beam in the Bragg method by a beam of electrons. The apparatus was built and mostly assembled before the results of Davisson and Germer were published. Although the results obtained in this experiment were not as accurate as those of Davisson and Germer, they seemed worth putting forward because they confirm the theory, using a different crystal and a Bragg method of analysis*.

Apparatus and Method of Experiment.

The apparatus was essentially similar to a Bragg X-ray spectroscope, the beam of X-rays being replaced by a beam of electrons. The arrangement of the filament and slits is shown in figs. 1 and 2. The important dimensions are, roughly, slits A to B 2.5 cm., slits E to F 1.4 cm., and slits B and E were about 1.4 cm. from the axis marked with a small circle. The size of these slits was about 1 by 4 mm. With this arrangement a slightly divergent beam of electrons (about three degrees) was defined by slits A and B. In order to obtain good definition of the reflected beam it would be advantageous to make the slits as fine as possible. Much finer slits than the above were tried when the apparatus was first set up, but it was found that the intensity of the scattered beam defined by slits E and F was too small to be measured satisfactorily. Hence the apparatus was dismantled and the slits enlarged to the above mentioned sizes. The accelerating potential was put on between the filament and slit A. The

* At the time of writing Davisson and Germer have published some preliminary results of experiments with a nickel crystal by the Bragg method. Proc. Nat. Acad. xiv. p. 317 (1928).

space around the crystal was sufficiently shielded to protect it from fields due to the charging of the surfaces of the containing glass bulb. While runs were being taken A, B, C, D, the crystal and framework of the apparatus, were kept at the same potential. A retarding potential was placed between slits D and E to analyse the reflected beam. The

Fig. 1.

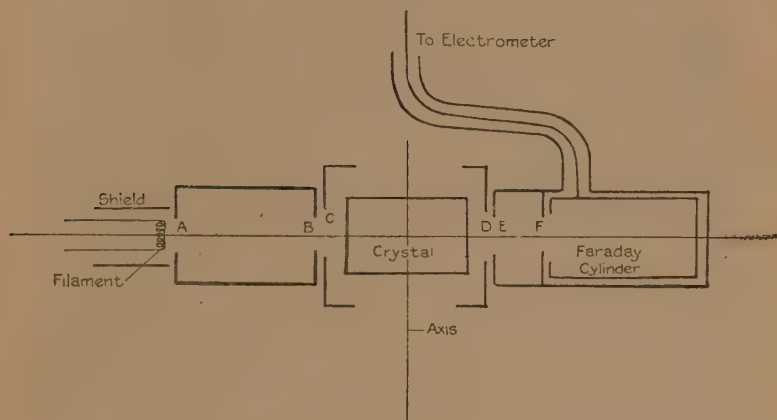
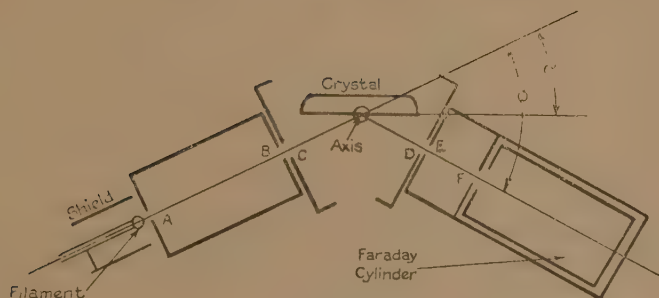


Fig. 2.



primary beam could be analysed by putting a retarding potential between slits B and C and using the whole frame and rest of the apparatus as a collector.

The crystal was loaned to the author by Professor G. I. Taylor. It was already cut with one face, about 7×14 mm. in size, parallel to a (111) plane. It was so arranged in the

apparatus that it could be rotated about an axis lying in that face, perpendicular to the direction of motion of the primary electron beam. The crystal was so orientated that one of the rows of atoms in its surface lay parallel to the axis of rotation, that is, one of the sides of the equilateral triangle formed by adjacent atoms in a (111) plane (face-centred cubic) of the crystal was parallel to the axis of rotation. The collector, which consisted of a Faraday cylinder inside an earthed shield, and the slits D, E, F, and G could be rotated about the same axis. The lead from the Faraday cylinder was carried up into the line of the axis of rotation in a quartz tube and out of the apparatus by a side tube in the same line. It was insulated with quartz except at the glass seal, and shielded by an aluminium tube outside the quartz all the way. The main frame was of aluminium. The shield around the filament and the first slit A were of mild steel as they got very hot during the experiments. The other slits were made of aluminium, except those in the collector, which were made of brass heavily nickel-plated. The bearings were steel on steel. The crystal and collector were rotated by means of an electromagnet acting on soft iron slugs in side tubes off the main containing bulb. These slugs were on the ends of shafts which turned worm and pinion drives. These in turn turned the crystal holder and collector independently about the same axis by means of a complicated system of bearings.

The fact that some of the parts of the apparatus, including most of the screws holding it together, were of steel meant that very low voltages could not be used with any accuracy owing to the probability of magnetic deflexion of the electron beams. However, the steel parts were kept as far away as possible from positions that would affect the results and were carefully demagnetized before being assembled. The magnetic rotating mechanism was also demagnetized between each reading by passing alternating current through the electromagnet and drawing it away from the apparatus slowly. Tests with a magnetometer showed that the field near the crystal, even under the worst conditions, could not have been much greater than the earth's field. As it was not intended in the first place to work below about 100 volts, and also because the steel parts in the apparatus would make compensation difficult, no attempt was made to compensate for the earth's field. A calculation shows that the error due to this could hardly be greater than about 1 degree for 100 volt electrons. This is the same magnitude as errors due to other causes.

The crystal face was prepared by polishing with fine emery, then etching with caustic soda until all traces of the polished layer were removed. It was then washed and dried and put in the apparatus without touching the prepared surface in any way. This surface, as would be expected after the etching, was rough and pitted. The electrons would not be expected to penetrate very far into the crystal without losing their identity with the primary beam or a considerable part of their energy. Since the reflexion effect, which the experiment was designed to study, is the interference or building-up of waves scattered by successive layers of atoms in the crystal structure, it is essential that the surface layers of atoms should be in the natural position defined by the crystal structure. Hence it was thought that it would be more advisable to leave the rough-etched surface exposed to the electron beam rather than to attempt to obtain a smooth surface. It is well known that an aluminium surface which has been exposed to air is always covered with a thin layer of oxide. However, it was hoped that this oxide layer would be so thin that it would not spoil the results, and that it would be advantageous in helping to prevent amalgamation with what mercury vapour got into the apparatus. In the experiments of Davisson and Germer the nickel crystal was treated much more rigorously. They heated their crystal by electron bombardment until the nickel distilled freely in vacuum. They found that their diffracted beam became very diffuse or disappeared if they allowed the pressure in their apparatus to increase to about 10^{-4} mm. This effect was ascribed to the absorbed gas molecules on the surface of the crystal. Considering the trouble they had with gas layers in the surface of their crystal it seems that no definite results should have been expected in the present experiment.

The metal parts of the apparatus, with the exception of the crystal, were vacuum ovened before assembly. The whole apparatus was assembled in a glass bulb about 5 inches in diameter with a $2\frac{1}{2}$ -inch neck and various side tubes to bring out the connecting leads and turning mechanism. The bulb was connected to a fast mercury-diffusion pump. This pump was backed by the Gaede type of rotary mercury pump and a Fleuss oil pump. Between the bulb and the diffusion pump there was a potassium-mercury trap, a liquid-air trap, and a mercury cut-off. The liquid-air trap was used while the apparatus was running. The potassium trap was intended to keep mercury vapour from reaching the apparatus overnight when there was no liquid air. The

pressure during the runs was of the order of 10^{-6} mm. Overnight it would increase to about 10^{-2} mm. This increase in pressure was probably due to the potassium trap giving off hydrogen. There was a phosphorus-pentoxide trap between the mercury vapour pump and the backing pumps, but this was separated from the apparatus overnight by the mercury cut-off. Possibly enough water vapour came off the walls and metal parts of the apparatus to produce this increase in pressure when it was reduced by the potassium. It was not due to a leak, as it did not occur before the potassium was run in. This effect made the intensity of the reflected beam slightly variable from day to day. However, as the object of the experiment was to find the position of the peaks rather than their intensity, it was not thought necessary to go to further refinements. Sets of curves for a given voltage were taken together during one continuous run, and repetitions showed exactly similar results.

The bulb was made of soda glass and so arranged on a stand that an electric oven could be lowered over it. This would heat the whole apparatus to about 300 degrees centigrade while the pumps were running. It was usually given about two days outgassing before taking a series of observations. The angles were read by means of a scale outside the glass bulb. The collector and crystal holder were arranged with a pointer so that the angle was read by the position of the line of sight defined by a point on end of the axle which supported the crystal holder and the pointer on the scale. The zero position could be found by adjusting the crystal so that the beam of light from the filament just grazed its surface. Variations in the thickness of the glass bulb would cause inaccuracies in the scale reading, but as the pointer and scale were as close to the glass as possible, the one on the inside and the other on the outside, the error would be reduced to a minimum. The angles could be read easily to better than half a degree. The peaks were much wider than this so more accurate measurements were quite unnecessary. The current was measured by timing the deflexions of a spot of light reflected from the mirror of an ordinary Dolezalek electrometer.

Results.

The procedure was as follows :—Setting the accelerating potential at say 122 volts, the crystal was set so that its surface made a small angle with the incident beam, then the current was measured in the collector at various points over

the range of angles (angle ϕ , fig. 2) from zero to about 120 degrees taken from the line of the incident beam as the zero line. It would be expected that sharp maxima would occur in the intensity distribution when the incident angle, that is the angle between the face and the incident beam, and the reflected angle were equal and connected with the voltage by relation (1) and

$$\lambda = \frac{h}{mv}, \text{ neglecting the relativity correction,}$$

$$\text{or } \lambda = \sqrt{\frac{150}{V}},$$

where V is the accelerating potential of the incident beam.

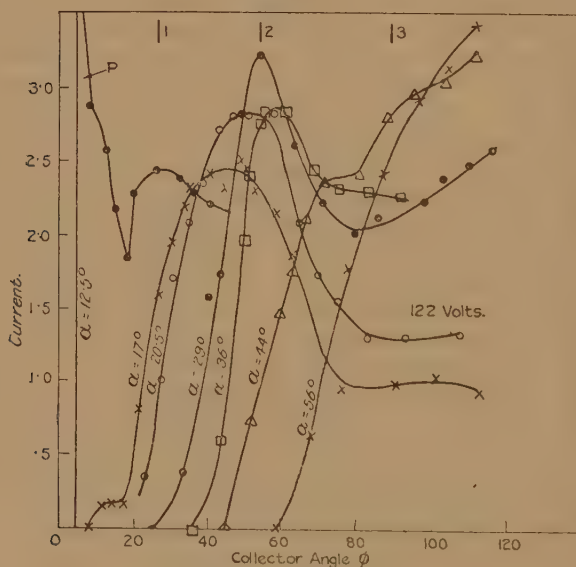
The electrons forming this peak should have the velocity of the incident beam. It was found that in order to get sufficient current in the collector it was necessary to have it from 20 to 40 volts positive with respect to the filament. This was due to the fact that the retarding potential was placed between slits D and E rather than just in front of the Faraday cylinder. These slow electrons would be deflected by any lack of symmetry in the retarding field and also any slight magnetic fields. Hence the analysis of the reflected beam is more a function of the position of the slits and of the retarding potential than of the velocity of the beam itself. This was shown in the following way:—The crystal and collector were set at the zero position so that some of the primary beam went past the crystal directly into the collector. An analysis of this beam by slits D and E showed that the current decreased roughly linearly for retarding potentials varying from about 20 to 30 volts below the accelerating potential to a retarding potential equal to the accelerating potential which stopped all the electrons. On the other hand, an analysis of the whole primary beam by a retarding potential between slits B and C showed that it was homogeneous to about 3 volts. This corresponds to the filament potential drop. Hence it seems reasonable to assume that very few electrons get into the collector except those which were allowed to pass through slit E with velocities greater than 20 volts. The primary bombarding current was about 10^{-7} amp., and the currents measured in the collector were of the order of 10^{-13} amp.

Fig. 3 shows a typical set of curves for 122 volts accelerating potential. They are plotted in the manner the readings were taken, that is, each curve represents the variation of the current in the collector for different values of the collector angle ϕ and one value of the crystal angle α .

The first high peak P which occurs when the crystal is set at a small angle is due to the fact that the incident beam was wider than the angular width of the crystal face when set at this grazing angle. As a result part of the primary beam gets past the crystal directly into the collector. This happens until the collector is turned sufficiently far around to be out of range of the primary beam. The short lines at the top represent the calculated position of the various orders of X-ray reflexion of the corresponding wave-length.

It is seen that there is a definite peak in the curve where the first order is expected, but it is so close to the incident

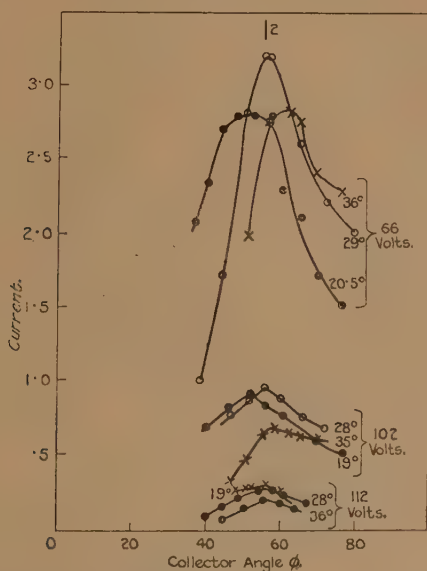
Fig. 3.



beam that its position cannot be located with any accuracy. However, there is a sharper peak at the expected position of the second order. This peak was examined very carefully for accelerating potentials of 122 volts. It was found that this peak could be located more accurately than the others. With a wide incident beam and a low resolving power due to the relatively small number of layers taking part in the reflexion the peak would be expected to cover a considerable range of incident angles. For this reason a peak occurs in the neighbourhood of the expected position for positions of the crystal anywhere near the correct reflecting angle.

However, the peak which occurs in a position such that the angle of incidence is equal to the angle of reflexion is always sharper and more intense than the others. Such a peak is seen in fig. 3 in the curve for which $\alpha = 28^\circ 5'$. This peak is taken as representing the reflected beam of electrons of 122 volts initial energy. The curves shown in fig. 3 were taken with the collector 37 volts positive with respect to the filament. That the peaks should be associated with the full accelerating voltage is shown by measurements of the position of the second order peak at different retarding potentials, as given in fig. 4. This figure

Fig. 4.

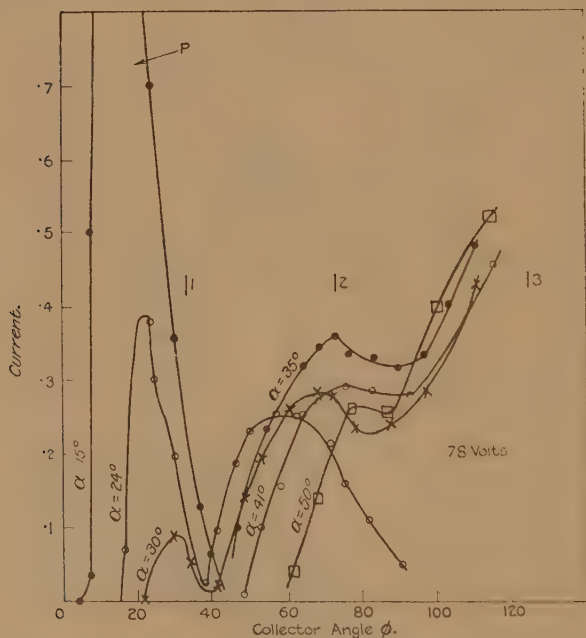


shows three curves for each retarding potential 85, 102, and 112 volts. One of the three was taken with the crystal set in as nearly as possible the correct position for wave reflexion and another curve was taken with the crystal set on either side of that position. The curves show that the position of the peak does not vary with the retarding potential, and therefore should be associated with the full accelerating potential rather than some potential between it and the retarding potential. The curves at the bottom of the figure, taken with a retarding potential of 112 volts, all show the peak in the same position. This is what would be expected with a finer analysis of the beam, but as the current was too

low to obtain very consistent readings no great significance should be given to this set. The third order position in fig. 3 is indefinite for a reason that will appear when the results obtained with higher voltages are discussed.

Fig. 5 shows a similar set of curves for 78 volts and a retarding potential of 65 volts. Here the first order appeared plainly, but is still at too small an angle to be located accurately. The currents were also so small as to be difficult to measure reliably. Lower voltages were tried with

Fig. 5.



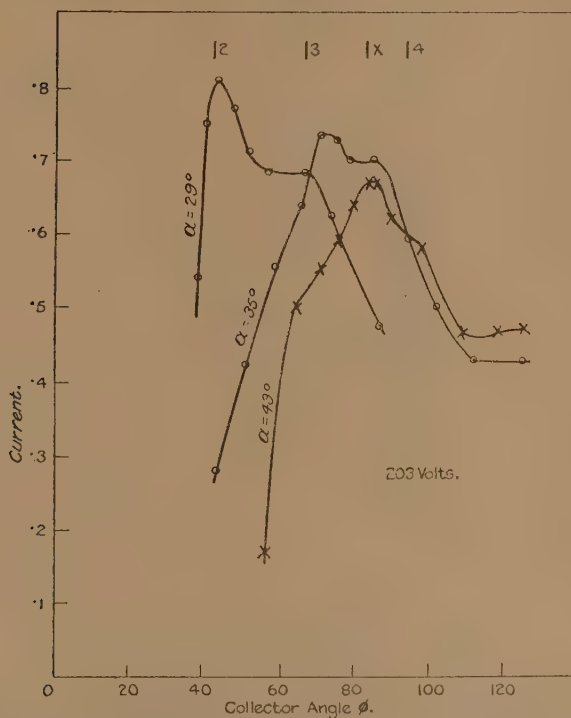
still lower retarding potentials, and peaks representing the first two orders were obtained. However, owing to the uncertainty due to the effects of small magnetic fields they can only be used to indicate that the peaks move in the right direction with varying voltages.

Higher voltages were tried, and in fig. 6 three curves are shown for an accelerating potential of 203 volts and a retarding potential of 164 volts. The curve showing the second order alone is not shown, but the existence of the second order is indicated by the curve with $\alpha = 29^\circ$. The third order is shown as a definite bump. Between the

third and fourth orders another peak occurs, marked X, which makes it impossible to separate these orders enough to give accurate results. Curves for 243 volts with a retarding potential of 306 volts show a similar peak. At this voltage the fourth order is plainly indicated, and a possible fifth order. These are shown in fig. 7.

Very little can be said about the relative intensity of the various orders. The first order is weak, no doubt due

Fig. 6.

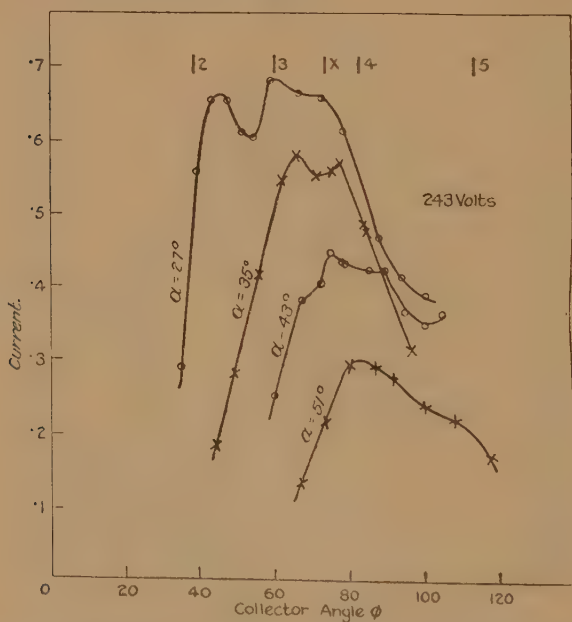


to the fact that it occurs at such small angles that only part of the primary beam is effective. The second is the strongest and therefore the one whose position can be located most accurately. The third is ambiguous because of the extra peak, and the fourth is very weak.

What causes the extra peak marked X is uncertain, but it is most likely due to contamination of the surface by gas or by the layer of aluminium oxide. Assuming that the extra peak is a first order reflexion the grating constant,

which it represents, would be $0.65 \text{ \AA}$. This is smaller than the accepted radius of an aluminium atom. However, on some of the curves for lower voltages there is a mere indication of another peak which might be the first order of this reflexion. This would then represent a spacing of $1.3 \text{ \AA}$. There is hardly enough information obtainable from this to associate it with any definite spacing in a corundum crystal, because it gives no information about the orientation except that the planes causing the reflexion are parallel to (111) planes in the aluminium crystal. The position of

Fig. 7.



these peaks is shown in Table II. The position of the peaks marked first order is very uncertain, as they are indicated only by the fact that for the lowest voltages tried one or two points were a little off the smooth line. A more accurate analysis of such peaks might give some information about the transition layer between aluminium and aluminium oxide.

Table I. gives a summary of all the peaks found which can be associated with the aluminium (111) plane spacing, $d = 2.34 \text{ \AA}$. Column 2 gives the angle θ in relation (1), which is half the angular position of the peaks shown in

figs. 3 to 7. Beside each angle is given the limits of possible error in locating the peak from the curves. Column 4 shows the wave-length calculated from the voltage, and

TABLE I.

Volts.	Angle of peak. θ .	Order. n .	Wave- length. $\sqrt{\frac{150}{V}}$.	Wave- length. $\frac{2d \sin \theta}{n}$.
56	25 $\pm$ 4	1	1.64	1.98 $\pm$ 0.30
56	42 $\pm$ 4	2	1.64	1.57 $\pm$ 0.14
62	21 $\pm$ 2	1	1.56	1.68 $\pm$ 0.15
62	42 $\pm$ 3	2	1.56	1.57 $\pm$ 0.14
78	16 $\pm$ 4	1	1.39	1.29 $\pm$ 0.32
78	37 $\pm$ 2	2	1.39	1.41 $\pm$ 0.07
83	16 $\pm$ 4	1	1.35	1.29 $\pm$ 0.32
83	36 $\pm$ 2	2	1.35	1.38 $\pm$ 0.07
122	14 $\pm$ 3	1	1.11	1.13 $\pm$ 0.24
122	28.5 $\pm$ 1	2	1.11	1.12 $\pm$ 0.04
164	25 $\pm$ 2	2	0.96	0.99 $\pm$ 0.07
164	45 $\pm$ 7	3	0.96	1.10 $\pm$ 0.14
203	21.5 $\pm$ 2	2	0.86	0.86 $\pm$ 0.08
203	35 $\pm$ 3	3	0.86	0.89 $\pm$ 0.06
203	50 $\pm$ 5	4	0.86	0.89 $\pm$ 0.06
243	23 $\pm$ 4	2	0.79	0.91 $\pm$ 0.15
243	33 $\pm$ 3	3	0.79	0.85 $\pm$ 0.07
243	46 $\pm$ 4	4	0.79	0.84 $\pm$ 0.06

TABLE II.

Volts.	Wave-length.	Angle.	Spacing.	Order.
56	1.64	36 $\pm$ 6	1.4	1
62	1.56	30 $\pm$ 6	1.5	1
203	0.86	43 $\pm$ 4	1.3	2
243	0.79	38 $\pm$ 4	1.3	2

column 5 the wave-length calculated from the angle and grating constant. This calculation assumes the index of refraction to be unity. It should be noted that the most accurately measured peak is the second order peak at

122 volts. Considering all sources of inaccuracies the possible error for this peak should not be greater than about 7 per cent.

Discussion.

The results of this experiment indicate that electrons can be diffracted by a crystal grating in the manner suggested by the wave theory. Table I. indicates that they agree with the theory within the accuracy of the experiment. This fact does not agree with the results of Davisson and Germer⁽²⁾. They found two types of diffracted beams. The first type is due to rows of atoms in the surface layer of the crystal acting as a plane diffraction grating. These are spoken of as surface diffracted beams. The second are those which correspond to Laue X-ray beams, as explained previously. These are depth diffracted beams, or considering a set of planes in the crystal as reflecting the waves when the angle and wave-length are such that they satisfy relation (1), they may be called depth reflected beams. These so-called depth diffracted beams, in the case of Davisson and Germer's experiment, may also be considered as positions of maximum intensity in the surface diffracted beam. Such maxima exist because more layers than one are effective in producing the beam. If a large number of layers was effective the beams would be all suppressed except the one at the position of this maximum. These depth diffracted beams should occur in the same directions as Laue X-ray beams of the same wave-length. The results of Davisson and Germer did show a set of depth diffracted beams arranged with a three-fold symmetry around the direction of the incident beam corresponding to a set of X-ray beams. However, they did not occur at the same angles that X-ray beams of the same wave-length would have occurred. They could be made to fit the corresponding set of X-ray beams by assuming a contraction of the crystal in the direction of the incident beam by a factor of about 0.7. This contraction factor varied for different beams. Patterson⁽³⁾ pointed out that by a different association of the electron beams with the Laue beams the two could also be made to agree by assuming an expansion factor in the same direction.

Eckart⁽⁴⁾ and Bethe⁽⁵⁾ have suggested what seems to be a much more satisfactory explanation of the difference in position between electron beams and corresponding X-ray beams. It is the assumption of an index of refraction for the de Broglie waves in the metal. Bethe shows that the existence of this index of refraction may be due to the

surface potential of the metal by the following reasoning. A more complete expression for the wave-length is

$$\lambda = \frac{h}{\sqrt{2m(E - V)}}$$

where E is the kinetic energy of the incident beam and V may be taken as the potential through which the electron must pass in going through the surface of the metal. From this it is easily seen that the refractive index is

$$n = \frac{\lambda_{\text{vac}}}{\lambda_{\text{metal}}} = \sqrt{1 - \frac{V}{E}}.$$

Now in order to prevent free electrons from streaming out of the metal the surface potential must be in a direction which accelerates the electron as it passes in through the surface and retards it as it passes out. This would mean that the velocity of the electron would be increased, hence the phase velocity decreased and the wave-length decreased. This means that the index of refraction should be greater than unity. This index of refraction should also vary with the accelerating potential. Using the results of Davisson and Germer, Bethe has calculated the value of the surface potential and obtained an average value of about 15 volts. He also points out that this is the order of the value expected on the Sommerfeld theory of conduction. In Davisson and Germer's later results, using a Bragg type of reflexion, they show some uncertainty as to the order of their peaks and give two sets of refractive indices, one greater and the other less than unity. The set having values greater than unity is probably the correct value. The indices vary from 1.14 to 1.01 for voltages from 28 to 585. A calculation of the surface potentials from this data gives an average value of about 14 volts.

The results of the present experiment fit the theory assuming an index of refraction of unity. Assuming an error equal to the estimated accuracy of the experiment (7 per cent.) for the second order peak at 122 volts, the refractive index would be 1.013. This would correspond to a surface potential of between three and four volts. The other peaks are not sufficiently accurate to give a reliable estimation of the surface potential. If the supposed second order peak were really a third order the surface potential would be about 35 volts. No matter which way one takes it, it seems unreasonable that there should be such a difference between nickel and aluminium.

There are possible explanations of the divergence between the results of the present experiments and those of Davisson and Germer, but they can all be ruled out with a fair amount of certainty. It might be that the residual magnetic fields in the present experiments were stronger than it was thought. Considering the precautions taken this seems very unlikely. Again, no correction was made for the diffuse background scattering, as the curves did not give sufficient information about it. It is, however, unlikely that such a correction would change the position of the peaks sufficiently to account for the divergence. It is also conceivable that the magnetic properties of the nickel crystal in the experiments of Davisson and Germer have some effect on the results, but it is very doubtful if such an effect would be noticeable as the fields would have to be very intense and so arranged that they would not interfere with the three-fold symmetry

Summary.

Experiments have been performed in which electrons have been reflected by the planes of an aluminium crystal in the manner suggested by the wave theory. The apparatus was similar to a Bragg X-ray spectroscope having the beam of X-rays replaced by a beam of electrons. It would be expected that a beam of electrons would be reflected in a manner analogous to X-rays when the accelerating potential, spacing constant of the crystal, and angle of reflexion were connected by the usual relations

$$\lambda = \frac{h}{mv}$$

and

$$n\lambda = 2d \sin \theta.$$

Four different orders of reflected beams were found whose position agreed with that predicted by theory within the accuracy of the experiment. Two orders of another set of beams were found, which are attributed to aluminium oxide or some other contamination of the surface of the crystal. A comparison is made between these experiments and those of Davisson and Germer (Phys. Rev. xxx. p. 705, 1927), who obtained different results with a nickel crystal. Their results differed from those predicted, but could be explained by the assumption of a refractive index.

In conclusion I would like to thank Prof. G. I. Taylor for making this experiment possible by lending me the

aluminium crystal with the required information about the position of its principal planes. I should also like to thank Prof. Sir Ernest Rutherford and Dr. J. Chadwick for interest and advice.

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- (2) Davisson and Germer, 'Nature,' 16th April, 1928, and Phys. Rev. xxx. p. 705 (1927).
- (3) Patterson, 'Nature,' cxx. p. 46 (1927).
- (4) Eckart, Proc. Nat. Acad. xiii. p. 519 (1927).
- (5) Bethe, *Naturwissenschaften*, xix. p. 333 (1928), and xviii. p. 786 (1927)

LXIX. *The Raman Spectra of Scattered Radiation.* By R. W. WOOD *. (Communication No. 7 from the Loomis Laboratory, Tuxedo.)

[Plate IX.]

THE very important and surprising discovery recently announced by Professor C. V. Raman and K. S. Krishnan opens up a new field in the study of molecular structure.

They found that if various transparent media, such as fluid organic compounds, crystals, and even water, are illuminated with monochromatic light, the spectrum of the light scattered by the medium shows, in addition to the line of the illuminating radiation, other bright lines the wave-lengths of which depend upon the nature of the medium. This at first sight might appear to be no different from fluorescence, but a closer inspection, as Prof. Ramsay showed, compels us to admit that the phenomenon is quite different and wholly new.

The difference may be well illustrated by the case of crystalline quartz, which is one of the substances which I have studied and which will be more fully described later. This substance, when illuminated by light of practically any wave-length in the region below the green mercury line, gives a companion line of wave-length greater than that of the exciting line (about 90 Å.U. in the case of excitation by

* Communicated by the Author.

the violet mercury line 4358). If the spectrum of the scattered light is photographed with a quartz spectrograph, we find every strong line or group of lines reproduced exactly by faint lines or groups of lines about $90 \text{ \AA.U.}$ on the long wave-length side. Now Raman has shown that the frequency difference between the companion line and the exciting line is constant, and equal to the frequency of an infra-red absorption band. This means that the light-quantum gives up a portion of its energy to the molecule, raising it to an excited state, and then passes off with diminished energy, recording itself in the spectrograph as a line of greater wave-length. An explanation of the phenomenon on the classical theory would have been difficult, to say the least, and it appears to me that no more convincing proof of the quantum theory of light has been found up to the present time. The line which I have found with quartz corresponds to the absorption band at 21μ . Two other lines, much fainter and closer to the exciting line, indicate absorption bands at 49 and 80μ respectively. No trace of a line corresponding to the band at 8.5μ has been found up to the present time. This is perhaps to be expected, as this band would correspond to a higher state of excitation which would be less probable than excitation to lower vibrational states. My spectrum of the quartz emission shows Hg 3125-3131 and 3650, 3654, 3663 beautifully duplicated. In the case of benzol, Raman found that a line of shorter wave-length than that of the exciting line was also present with the same frequency difference (measured against the exciting line) as was the case with one of the lines of longer wave-length. This could mean only that the impinging quantum of violet light (4358) gathered up some energy from a molecule already in an excited state, and then rebounded as a quantum of greater energy which recorded itself on the ultra-violet side of the exciting line. The line was so faint that it did not appear on the reproductions of his photographs, but a curve made with a recording photometer showed a very small hump at the right place. Employing higher dispersion I find a double line at this point, a matter which will be more fully discussed later on. In the case of carbon tetrachloride I find anti-Stokes terms (shorter wave-length lines) almost as strong as the corresponding lines of longer wave-length, the group being reproduced as a "mirror-image," regarding the exciting line as the mirror (Pl. IX. fig. *b*). With improved methods of illumination I have been able to record the stronger Raman lines with an exposure of only a few minutes.

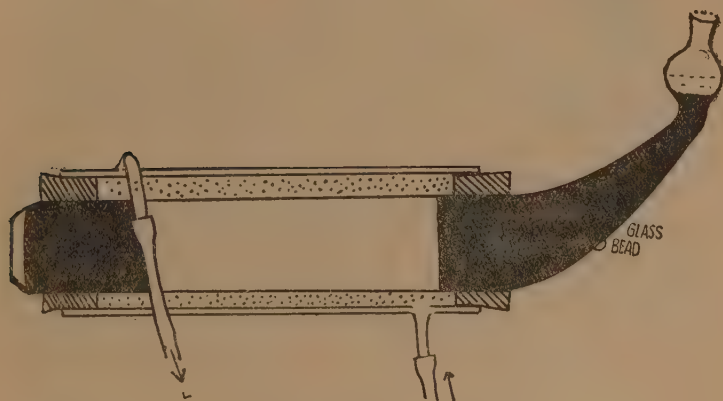
Apparatus and Methods.

Raman illuminated his fluids in spherical glass bulbs, concentrating the light of a mercury arc at the centre of the bulb by means of a large lens, and photographed the spectrum of the illuminated area viewed end-on.

This method of excitation is very inefficient in comparison with that which I have employed in recent investigations of resonance spectra ; in which the arc is brought into close proximity with the resonance tube.

The apparatus used in the present work is the outcome of a number of trials, and can hardly be improved upon. The illumination is so powerful that the strongest Raman lines can be photographed with an exposure of a few minutes.

Fig. 1.



The tube is water-cooled, and if filters are to be employed for the removal of certain portions of the spectrum of the exciting light, the colouring material can be dissolved in the water operating the cooling system.

It is shown in fig. 1, and consists of a glass tube of 3 cm. internal diameter, blown flat and rather thick at one end, like the bottom of a bottle, and drawn off into an oblique cone at the other. The flat bottom is ground plane and polished, or is made sufficiently good optically by cementing a thin cover-glass to the ground surface with Canada balsam. Bulbs were used at first, but they act as spherical short-focus lenses when the tube is filled with liquid and are unsatisfactory, since only a single section of the tube can be brought to a focus. A small bead of glass is fused into the wall of

the sloping cone as nearly as possible in coincidence with the tube's axis. This bead, when backed by a lamp, is visible as a bright star when viewed through the other end of the tube, and is of great assistance in adjusting the tube parallel to the axis of the collimator—a very important matter. With the tube filled with liquid, it is impossible, without the bead, to send a ray of light down its axis, on account of refraction by the oblique wall.

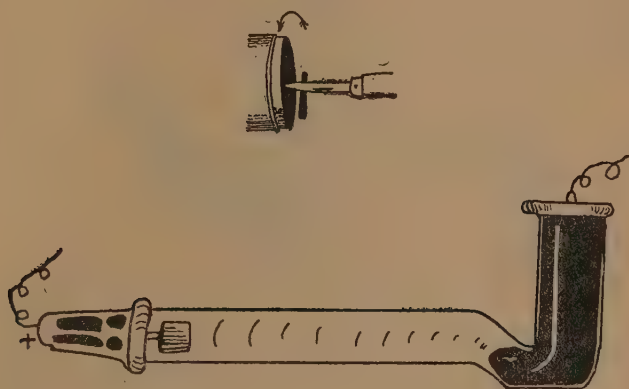
The tube is painted on the outside with black paint (the new celluloid enamel paint for automobiles is best), as shown in fig. 1, taking care not to cover the bead, and surrounded by a second glass tube provided with side tubes for the in- and out-flow of the water. The seals at the ends are made from rubber stoppers in the following way, a method not as well known as it should be. A stopper of size sufficient to allow it to be slipped easily for two-thirds of its length into the large tube is inserted snugly into a short length of brass tubing, preferably made slightly conical on the inside to fit the stopper. This is mounted in a lathe and spun rapidly. A pen-knife with a long thin blade made very sharp at the point is moistened with glycerine, and rested, cutting-edge up, on a tool support adjusted parallel and very close to the protruding face of the stopper. The point is now pressed lightly against the stopper, marking a circle, which should be of a diameter equal to that of the inner tube. The blade is now pressed through the stopper, taking care to keep it parallel to the axis of rotation and tangential to the circle which is being cut. It will go through the stopper in a few seconds, giving a clean-cut ring with a central plug, which is easily pushed out after removing the stopper from the brass tube. It is possible to make rings a millimetre or two in thickness from stoppers 4 or 5 cm. in diameter. The position of the knife blade with respect to the rotating stopper is shown in fig. 2.

The exit tube for the water must be on the top of the outer tube, and be bent sharply down as shown, so that the tube of the mercury arc can be brought down to within a centimetre or two of the tube, as shown in fig. 1. Without the cooling system most of the fluids studied would have been raised to the boiling-point in a few minutes.

Water was delivered from an iron pail with a brass tube soldered through the side close to the bottom, and a glass stop-cock in circuit with the rubber tube controlled the flow, insufficient cooling being indicated by the rise of the fluid in the small bulb surmounting the oblique cone. The quartz mercury arc must be mounted in some type of support free

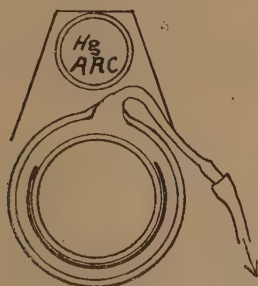
from metal supports on the underside, so that it can be brought down almost in contact with the upper surface of the water jacket. Two reflectors augment the illumination, one of them above the arc, and resting on the quartz tube,

Fig. 2.



the other, bent to a hemi-cylinder of slightly less diameter than that of the inner tube, clamps around the latter on the underside. These reflectors were made of very highly-polished sheet aluminium of about the thickness of writing-paper (a commercial product). An alternative method

Fig. 3.



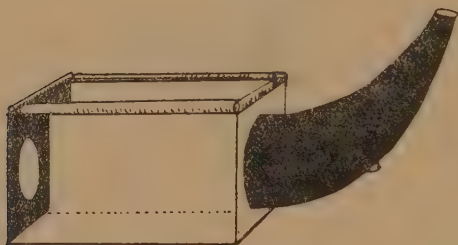
would be to silver the inner tube on the lower surface. The disposition of the reflectors is shown in fig. 3.

By this arrangement practically the entire emission of the quartz arc is thrown into the inner tube, and the intensity is

still further increased by reflexion back from the cylindrical reflector.

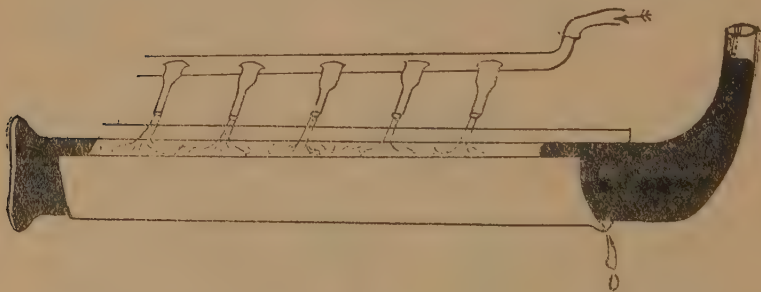
In the case of solids, such as quartz, calcite, or glass, the method employed is shown by fig. 4. The front face of the block is painted black, with the exception of a circular aperture and a bent cone of glass cemented to back face with

Fig. 4.



piccin wax: this cone is filled with glycerine and is painted black; a glass bead is provided for collimation. On the upper face four small glass rods are attached with surgeon's tape: these form a wall to retain the pool of water, constantly renewed by a small stream, which keeps the block cold. The block is mounted at a slight angle on a sheet of

Fig. 5.



the reflecting aluminium, so that the water overflows on the cone side and the front window remains clear, the water being carried away by a tin gutter. A third and simpler arrangement is shown in fig. 5. This was employed in the excitation of fluids in a quartz tube by the total radiation of the arc. The end of the tube was blown out into a thin bulb the front of which was then flattened in the flame. The

tube rested in a cylindrical gutter of the highly reflecting aluminium previously described, the cooling being effected by five jets of water which played continuously against its upper surface. This tube, like the block of quartz, was mounted at a slight angle to prevent the water from running out of the upper end of the gutter. The water-jet tubes point in a nearly horizontal direction just under the edge of the aluminium reflector which covers the lamp. The brilliancy of the light scattered by pure dust-free liquids under these conditions is very surprising, and it is hard to believe that the fluid is not turbid.

The aiming of the spectrograph is a matter of great importance if scattered light from the walls of the tube is to be avoided. It is best accomplished in the following way. Two diaphragms are formed by perforating two rather large squares of black cardboard with holes about 1 cm. in diameter. These are mounted in clamp stands about 30 cm. apart, with the holes in line with the axis of the tube. An incandescent lamp with a frosted bulb is placed close to the glass bead, and the screens adjusted so that the bead is visible centrally placed when viewed through the two holes. The spectroscope is now placed with its slit about 20 cm. from the first screen, the collimator pointing through the two holes at the illuminated bead. Before bringing the spectroscope into place, it is well to light the arc and make sure that only the illuminated fluid is visible through the two holes when the eye is moved about over the first hole. Next, bring the eye up to the region where the spectrum is focussed, and, with the slit wide open, adjust the instrument to such a position that the illuminated bead is seen exactly at the centre of the camera lens. It will be coloured, of course, the colour depending upon the position of the eye. Remove the incandescent lamp and mount a lens of about 18 cm. focus close to the first screen. The lens forms an image of the hole in the second screen on the slit of the instrument, and on placing the eye at the focus, the whole field of the instrument should appear illuminated with green light when the pupil of the eye is in the position of the green mercury line. The slit is now closed and the exposure made. This method of aiming a spectroscope will be found useful in the case of many other investigations.

Experimental Results.

An important point to be settled is the relative intensity of scattering for the exciting and modified wave-lengths.

To accomplish this we must be sure that only light scattered by a dust-free and pure fluid enters the spectrograph. I have made only a rough preliminary examination of this point in the case of some of the strongest Raman lines, and found that the ratio of scattering is of the order 1 : 500. This determination was made by making a series of exposures of varying time and picking out the two which gave the modified and unmodified lines of the same intensity. We will now take up the results obtained with a selected few of the liquids and solids examined up to the present time. Wave-length determinations have not been made of all of the plates, as preparations are now under way for photographing the spectra with a prism spectrograph of 40 foot focus. The photographs were made with a constant deviation Bausch and Lomb one-prism spectrograph of 50 cm. focus, with a comparison spectrum of iron running across the centre. The spectrograph was kept at a constant temperature by a toluene thermostat, as in some cases exposures of several hours were necessary.

It was at once apparent that still higher dispersion was desirable, as some of the lines were found to be bands sharp on the long wave-length side and shaded off towards the violet.

Turning now to Pl. IX., we find at the top the spectrum of the quartz mercury arc used for the excitation of the materials. It was much over-exposed for the purpose of bringing all of the fainter lines, which otherwise might be mistaken for Raman lines, on the spectrograms. Below this is the spectrum scattered by carbon tetrachloride, which has been reproduced of full width, showing the lines both above and below the iron comparison spectrum. The other prints have been trimmed narrower, showing iron on one side only.

Carbon tetrachloride.

This is perhaps the most striking photograph of all, on account of the great intensity of the modified lines of wave-length shorter than that of the exciting line. Immediately to the right of the 4358 line of mercury we find a strong triplet with the lines spaced thus |||, while to left, and symmetrically placed, the same triplet reversed thus |||, this being the anti-Stokes group. We find in addition a close double line further along towards the green region. This same complete set of lines will also be seen to the right of the violet 4047 line, the Raman lines being indicated by

ink dots below the spectrum. Still more remarkable is the appearance of the groups, both Stokes and anti-Stokes, excited by the green line 5461, also indicated by dots. Raman reported that he found no trace of excitation in any case by this line, as might be expected from the Rayleigh law of scattering, but in the case of carbon tetrachloride, chloroform, and some other substances the green line produces strong scattering of modified lines. One of the anti-Stokes lines is in coincidence with a very faint mercury line, which appears much intensified by the superposition of the Raman line. The wave-lengths and frequencies are given in the following table :—

Carbon Tetrachloride.

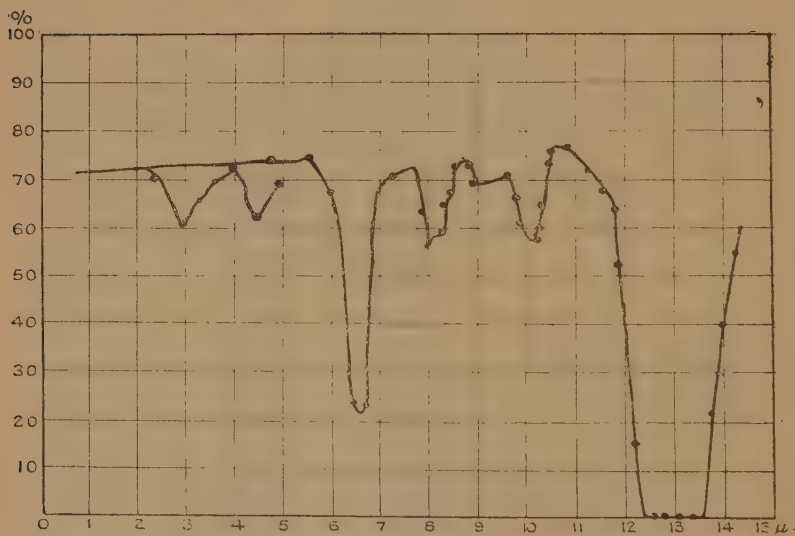
λ of Exciting Line.	Freq. of Exciting Line.	λ of Modified Line.	Freq. of Mod. Line.	Frequency Difference.
4046.8	247039	4082.0	244909	2130
		4098.3	243932	3107
		4127.7	242491	4548
		4174.4	239488	7551
		4179.6	239190	7849
4077	245161	4155.0	240606	4555
4358	229383	4317.3	231561	—2178
		*4400.2	227199	2184
		4299.45	232523	—3139
		*4419.0	226240	3143
		4272.6	233984	—4601
		*4447.05	224805	4578
		*4507.35	221798	7585
		*4513.7	221484	7899
4347	229953	4388.8	227794	2159
		4407.5	226823	3130
		4435.6	225386	4567
4339	230393	4426.9	225829	4564

The triplet and doublet previously mentioned are indicated by stars. We find in this table the wave-lengths of the modified lines excited by the fainter mercury lines in the vicinity of 4046 and 4358 (shown on the upper spectrum of Pl. IX., and better resolved because of less exposure in the lower spectra). The frequency differences in the right-hand columns have been arranged slightly

displaced, so that those which belong together can be seen at a glance. Anti-Stokes lines are indicated by a minus sign.

We see from the table that we are dealing only with the five frequency differences corresponding to the five lines previously mentioned. The maximum and minimum values are 2184 and 2130, 3143 and 3107, 4601 and 4548 for the triplet, and the average of all values for the doublet are 7570 and 7875, these two last being the frequencies corresponding to wave-lengths 13.2μ and 12.2μ . Now, Coblentz's

Fig. 6.



curve of the infra-red absorption of carbon tetrachloride shows complete absorption between 12.5μ and 13.5μ . This curve is reproduced (fig. 6).

The close double line at λ 4507 and 4513 thus corresponds to this absorption band, and proves that it is in reality a double band. The other three frequency differences correspond to absorption bands at 46μ , 32μ , and 22μ , a region difficult or impossible to investigate by absorption methods. An attempt to find these by the method of residual rays will be made in the autumn, if they cannot be found in the literature, which seems unlikely.

I have given the full set of values in this and some of the following cases, as they form such a complete verification of

the theory of Professor Raman, and show the value of the method for the investigation of the remote infra-red absorption region by the study of modified lines in the visible part of the spectrum.

Chloroform.

The modified lines of this substance are shown in spectrum *c* of Pl. IX. They occur in pairs, the anti-Stokes terms are strong, and they are excited by the green line as well as by the violet lines. The values are given in the following table:—

Chloroform.

λ of Exciting Line.	Freq. of Exciting Line.	λ of Modified Line.	Freq. of Mod. Line.	Frequency Difference.
4347.5	229953	4397.4	227343	2610
		4417.7	226299	3654
		4477.1	223296	6654
4358	229383	4408.8	226756	2627
		4308.4	233040	—2657
		4427.1	225716	3667
		4289.9	233040	—3657
		4489.4	222684	6699
		4234.3	236100	—6717
		4507	221815	7658
4046.8	247039	4089.7	244448	2591
		4159.1	240369	6670
		4174.1	239465	7574
4077.8	245161	4191.9	238488	6673

The average values of the frequency differences are 2621, 3655, 6682, and 7571, corresponding to infra-red absorption at 38.15μ , 27.93μ , 14.96μ , and 13.20μ respectively. Coblentz gives complete absorption at 12.5μ .

Benzol.

Coming now to a ring molecule, we find that the modified lines of shorter wave-length than that of the exciting line are absent or so faint that they come out only with very long exposure. Spectrum *d* was made with this substance. To bring out the faint lines it is necessary to distil the

substance, as it contains an impurity which causes a strong continuous spectrum (probably fluorescence) in the blue and green region.

If a spectrogram is made of the residue left in the flask, this spectrum is so strong that the Raman lines are practically wiped out.

It was with benzol that Raman found his anti-Stokes line at 4178.5, so faint, however, as to be almost invisible, and reproduced in his paper only by a very small hump on the microphotometer curve. With long exposure I have found two lines at this point very close together, one of wavelength 4177.3 excited by 4358, and another of $\lambda = 4190$ excited by 4046.

The source of excitation of these lines was determined by filtering out the 4046 line from the light of the arc by adding chromate of potassium (*not* bichromate) to the water supplying the cooling system. The amount to be added depends upon the thickness of the layer of water between the tubes, and is best determined by adding increasing amounts to the water in the pail until the 4538 line scattered by the liquid in the inner tube shows a trace of weakening. This can be done visually or, better, photographically. Under these conditions 4046 is practically removed. The 4358 line can be removed, permitting excitation by 4046 and lines of shorter λ by means of fluorescein. The out-flow runs into a second pail on the floor, from which the upper pail is replenished. These two substances were used in the case of a number of other substances in which there was doubt about the origin of the modified lines.

On examination of the benzol spectrogram with a high-power magnifier, it was at once evident that the strong line at 4618.8 (indicated by a dot) was in reality a sharply-shaded band, very intense and sharp on the side towards the red. This line is originated by the 4046 excitation, as was found by Raman and verified by the chromate of potassium filter.

Benzol was the only substance for which wave-lengths were determined by Raman (at least in his first paper), and as they were made without an iron comparison spectrum from the mercury lines as standards, they are remarkably good. The values given in the following table are probably a little more accurate, and eight or ten lines not found by Raman are given. The increase of accuracy results from the use of about double the dispersion employed by Raman and the presence of the iron comparison spectrum.

Benzol (with intensities of stronger lines estimated).

λ of Exciting Line.	Freq. of Exciting Line.	λ of Modified Line.	Freq. of Mod. Line.	Frequency Difference.
4339	230393	4533.5	220514	9879
4347.5	229953	4542.1	220101	9852
4358.3	229383	4476.7(3)	223316	6067
		4525.8	220896	8487
		4555.8(5)	219439	9944
		5029.6(4)	198768	30515
		4681.7	213538	15845
		4687.1	213297	16086
		4594.7(3)	219581	11702
		4177.3	239322	-9939
4046.8	247039	4147.7	241024	6015
		4190.5	238568	8471
		4215.7(10)	237142	9897
		4090.8	244382	2654
	(band)	4618.8(8)	216446	30593
		4322.9	231261	15778
		4327.3	231026	16013
4077.8	245161	4180.9	239116	6045
		4215	239142	8019
		4248.9(4)	235289	9872
		4123.7	242491	2670
		4657.5	214648	30513
4108.1	243353	4282.2	233459	9894
3650	273883	4109.7	243317	30566
3654	273535	4115.1(4)	242945	30590
3662.9	272937	4125.5(4)	242326	30605

The last three lines represent the reproduction of the mercury ultra-violet triplet in the violet region, the first member falling a trifle on the long wave-length side of the mercury line 4108. It is scarcely resolvable from this in the reproduction.

The frequency difference 30564 corresponds to an absorption band at 3.27μ (Coblentz gives 3.25μ), 15812 to a band at 6.30μ , and 16050 to a band at 6.23μ (Coblentz 6.25μ).

Toluol and Monochlor benzol.

Raman spectra of these two compounds are shown on Pl. IX. (*e* and *f*). The chlorine compound became milky under the action of the light, and consequently the mercury lines were very strongly scattered, none of the lines to the right of 4915 Hg being Raman lines. The spectra are quite similar in appearance, owing to the similarity of the two molecules, chlor benzol being regarded as toluol with the CH_3 replaced by chlorine.

Partial determinations only of the wave-lengths of these substances have been made at the present moment, and it does not seem worth while to publish them, as it is expected that spectra under vastly higher dispersion will be obtained very shortly. Benzol, toluol, and xylol appear to have lines in common.

The spectrum of xylol is reproduced (spectrum *g*) excited by the total radiation of the arc, and spectrum *h* excited with 4046 removed by the chromate of potash. As will be seen, some strong lines in the group to the right of 4358 are due to 4046. Below these are reproduced spectra of ether, methyl alcohol, and ethyl alcohol. Spectra have also been made of bisulphide of carbon, sulphuric acid, water, nitrobenzol, and a number of other substances, but the plates have not yet been measured.

Quartz.

The lines scattered by a large block of very clear crystal quartz are reproduced (spectrum *l*), the Raman lines being indicated by dots. The frequency difference for these three lines (wave-lengths 4448.3, 4397.4, and 4382) are 4632, 2040, and 1246, corresponding to absorption bands at $21.58\ \mu$, $49\ \mu$, and $80.3\ \mu$.

Residual-ray methods show a band of metallic absorption at $20.7\ \mu$, which is given by the 4448.3 line. So far as I know, definite bands of longer wave-length have not been observed. Quartz is moderately transparent at $56\ \mu$ and also between 100 and $300\ \mu$.

No trace has been found as yet of a Raman line corresponding to the well-known absorption band at $8.5\ \mu$.

Calcite.

Modified lines have been obtained with calcite (Iceland spar) also. The frequency differences in this case were 10870, 17302, and 2802, corresponding to infra-red absorption at $9.19\ \mu$, $5.78\ \mu$, and $35.7\ \mu$. So far I have been able to find record only of bands at $11.3\ \mu$, $6.46\ \mu$, and $30.3\ \mu$.

Preparations are under way at the moment for a record with a very large and clear crystal with which observations can be made in several directions.

The observations on calcite were made with a very clear natural rhomb measuring $4 \times 5 \times 2$ inches, backed by a reflector and surmounted by a pool of running water.

The wave-lengths of the lines excited by 4358 are given in the following table, together with the corresponding absorption bands (calculated) in the infra-red. Such absorption bands as have been observed are given in the last column:—

Modified line.	μ (cal.).	μ (obs.) residual rays.
4386.45	68	
4387.35 } Barely resolved	65.9	
4389.15 }	62	
4412 (strong).....	35.67	30.3
4498.2 (faint)	14	11.3
4574.6 (very strong).....	9.18	6.46

The calculated absorption bands in this case are of considerably longer wave-length than those observed by the method of residual rays.

Rock-salt.

No lines have been found with rock-salt up to the present time.

In conclusion, I wish to express great obligation to Mr. H. M. O'Bryan, who determined the wave-lengths and rendered much assistance in picking out the lines which belonged together.

Loomis Laboratory, Tuxedo, N.Y.
Sept. 8th, 1928.

LXX. *The Equation of State of a Perfect Gas.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a paper that appeared in the June number of the Philosophical Magazine, the writer showed from thermodynamical considerations of the zero of entropy that the equation of a perfect gas, or the limiting equation of state

of the substance when the volume is infinitely large, is strictly

$$pv = MRT\xi,$$

where ξ is a function of the volume v , absolute temperature T , and mass M in mols. The proof may be given an improved form which will now be pointed out. The term $p(v_2 - v_1)$ in equation (3) may be written $p_2v_2 - p_1v_1$, where p_1 and p_2 denote the pressures in the condensed and vaporous states respectively. Equation (6), which applies to $T = 0$, may then be written

$$\left(\frac{\partial w}{\partial T}\right)_v = v_2\left(\frac{\partial p_2}{\partial T}\right)_{v_2} - v_1\left(\frac{\partial p_1}{\partial T}\right)_{v_1} = 0.$$

Now $\left(\frac{\partial p_1}{\partial T}\right)_{v_1} = 0$ at $T = 0$ (Phil. Mag. iv. p. 262, 1927),

and hence

$$v_2\left(\frac{\partial p_2}{\partial T}\right)_{v_2} = 0.$$

The rest of the argument is the same as before.

The result may also be obtained independently of considerations of the zero of entropy. The writer has shown (J. Franklin Inst. 206 (5) p. 692, 1928) that a mon-atomic gas at infinite volume near in temperature to the absolute zero has a maximum specific heat whose value is abnormally large, which depends on the fact, deductable from Clapeyron's equation, that the internal heat of evaporation at $T = 0$ is zero. Thus the specific heat c_v at constant volume is a function of the temperature, and this will therefore also hold for γ , the ratio of the specific heats. Now the temperature scale of a perfect gas thermometer coincides with the thermodynamical scale of temperature only if γ is a constant, and hence these scales strictly do not coincide. Therefore, if the temperature, as measured by the perfect gas thermometer, is expressed in terms of the temperature T on the thermodynamical scale, the equation of a perfect gas becomes

$$pv = RT \cdot \phi(T').$$

It can now be shown similarly as before that the function ϕ also involves the volume v .

Yours faithfully,
R. D. KLEEMAN.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

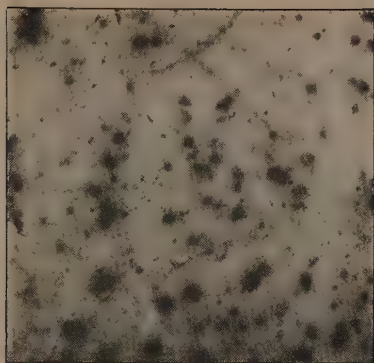


FIG. 4.

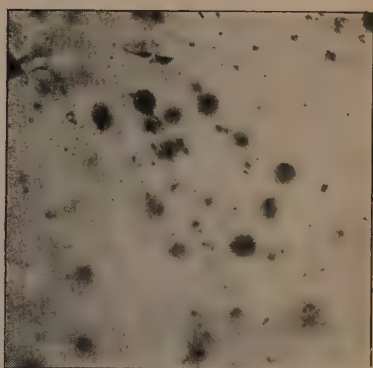


FIG. 5.

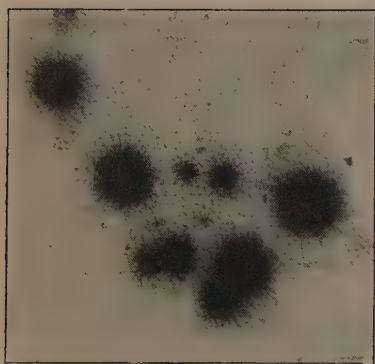


FIG. 6.

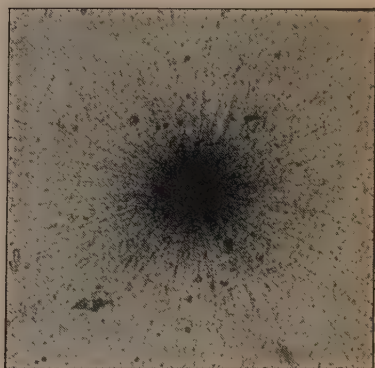


FIG. 7.

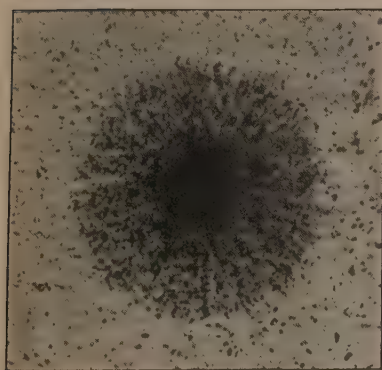


FIG. 8.

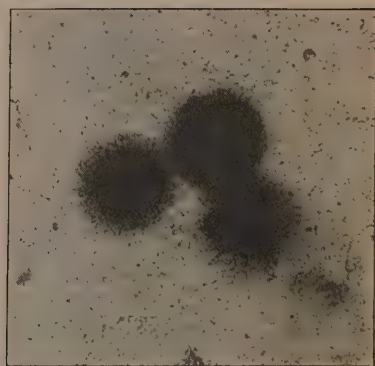
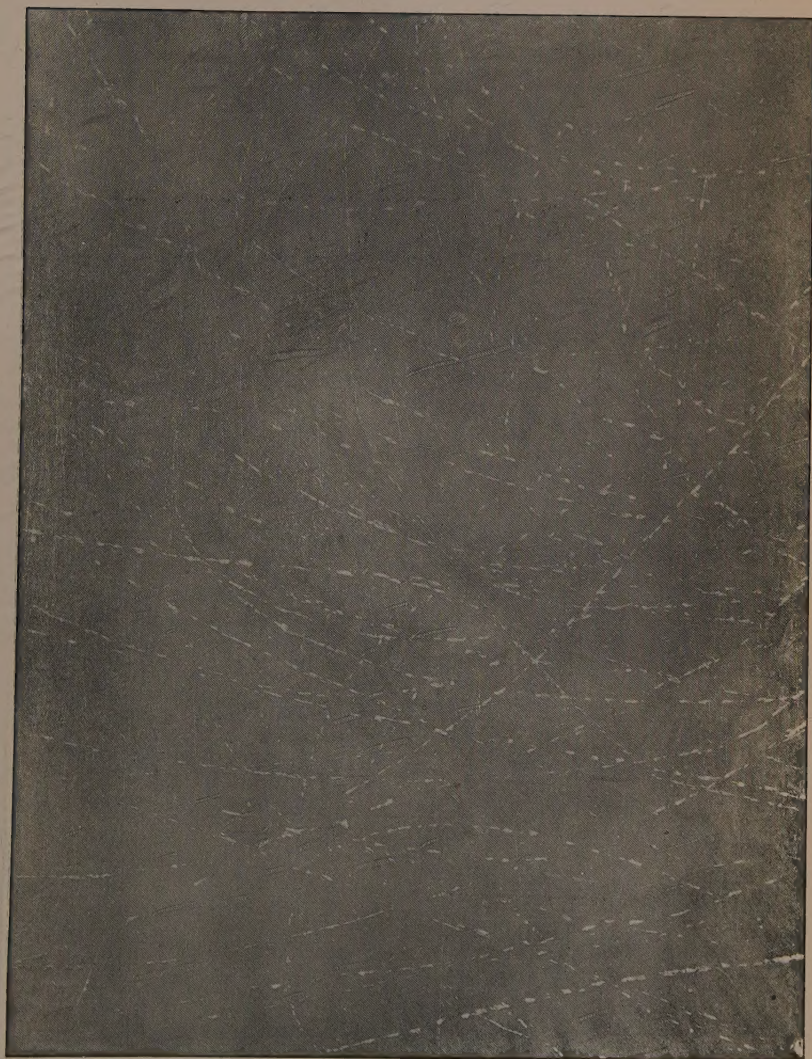


FIG. 9.

FIG. 3.



Wood.

4046.8

4077.8

4108.1

4339

4347

4358

